

# Synthesis and Thermal Stability of New Polynitrostilbenes

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New polynitrostilbenes were directly synthesised by the Knoevenagel condensation of aromatic aldehydes with nitrotoluenes. The differential scanning calorimetry results demonstrated that the introduction of an amino group and C=C double bonds could improve the thermal stability.

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## Introduction

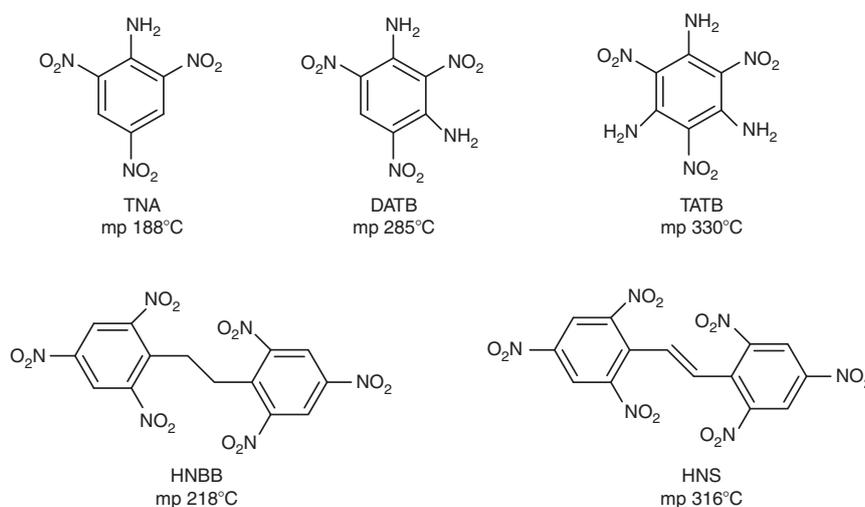
2,2',4,4',6,6'-Hexanitrostilbene (HNS) has played a significant role in the industrial, military, and space fields since it was synthesised by Shipp in 1964.<sup>[1–3]</sup> Because of its good thermal stability and detonation properties, considerable attention has been paid to new polynitrostilbenes with high melting points.<sup>[4–9]</sup> HNS has been derivatised with various functional groups such as halogeno, methoxy, methylamino, and amino groups.<sup>[5–7]</sup> In particular, the introduction of an amino group in a molecule adds energy to the crystal lattice, thus increasing the melting points of the resulting compounds.<sup>[6,10]</sup> The structures and melting points of trinitroanisole (TNA), 1,3-diamino-2,4,6-trinitrobenzene (DATB) and 2,4,6-triamino-1,3,5-trinitrobenzene (TATB)<sup>[11]</sup> are shown in Scheme 1: the existence of amino group(s) in these compounds improves their thermal behaviour.<sup>[12,13]</sup> Moreover, the C=C conjugated double bonds

are found to enhance the thermal stability as demonstrated by comparing the melting points of HNS (316°C) and hexanitrobibenzyl (HNBB) (218°C).<sup>[5]</sup> Inspired by these results, we have investigated the effects of the amino group and C=C conjugated double bonds on the thermal stability of new polynitrostilbenes, which are synthesised by the Knoevenagel condensation of aromatic aldehydes with nitrotoluenes.

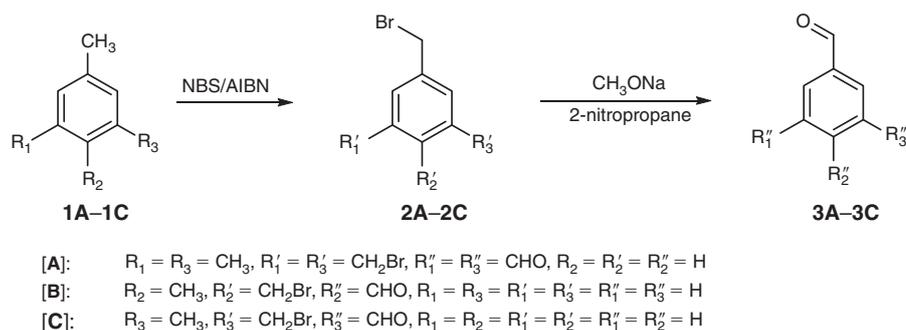
## Results and Discussion

### Synthesis of Polynitrostilbenes

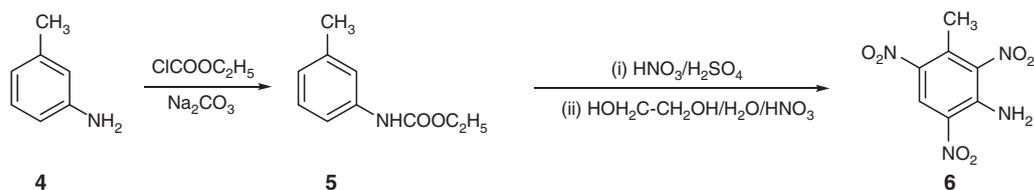
Mesitylene **1A** was brominated using *N*-bromosuccinimide (NBS) in the presence of azobisisobutyronitrile (AIBN)<sup>[14]</sup> to give 1,3,5-tris(bromomethyl)benzene **2A** in only a moderate yield. However, when NBS was added every 1.5 h along with AIBN three times, the yield was increased to 82.6%.



**Scheme 1.** Structural formulae of the five explosives trinitroanisole (TNA), 1,3-diamino-2,4,6-trinitrobenzene (DATB), 2,4,6-triamino-1,3,5-trinitrobenzene (TATB), hexanitrobibenzyl (HNBB) and 2,2',4,4',6,6'-hexanitrostilbene (HNS).



**Scheme 2.** Synthesis of multi-substituted benzaldehydes (*N*-bromosuccinimide: NBS, azobisisobutyronitrile: AIBN).



**Scheme 3.** One-pot synthesis of 3-amino-2,4,6-trinitrotoluene (ATNT).

Benzene-1,3,5-tricarbaldehyde **3A** was prepared upon treatment of **2A** with the 2-nitropropane carbanion<sup>[15]</sup> in a mixed solution of methanol and ethyl acetate. Compounds **3B** and **3C** (Scheme 2) were prepared by the same method.

3-Amino-2,4,6-trinitrotoluene (ATNT, **6**) was prepared under a one-pot process (Scheme 3) in 85.9% yield (23.2% yield<sup>[16]</sup>), which avoided the redundant separation process and purification of the intermediate **5**. ATNT **6** was synthesised via the nitration of *N*-(3-methylphenyl)ethylcarbamate **5** using nitro-sulfuric mixed acid, followed by hydrolysis with an alcohol–water mixture. It is worth mentioning that water was indispensable in the hydrolysis reaction of carbamates for its nucleophilic behaviour.<sup>[17–19]</sup> Among the various alcohol–water mixtures, involving methanol, ethanol, propanol, isopropyl alcohol, and glycol, glycol–water (3 : 1 in volume) could promote the reaction up to 85.9% yield at 95°C.

The synthesis of polynitrostilbenes was conducted by the condensation of aromatic aldehydes with TNT and ATNT. Benzaldehydes functionalised with weakly active halogen atoms could form corresponding nitrostilbenes in high isolated yield (entries 2–5 in Table 1). Moreover, the high reactivity of the carbon–halogen bond on the new nitrostilbenes might allow the introduction of such diversified functional groups as –OH, –NO<sub>2</sub>, –CN, –N<sub>3</sub>, etc. into the molecular structure,<sup>[20]</sup> thus giving new potential energetic materials. 4-Nitrobenzaldehyde with an electron-withdrawing nitro group showed low reactivity (entry 1 in Table 1). 4-Methylbenzaldehyde with electron-donating group reacted with polynitrotoluenes more easily (entry 6 in Table 1). Moreover, the structure of a representative polynitrostilbene **13D** was proved conclusively by single crystal X-ray diffraction analysis (Fig. 1).

It was interesting that the aldehydes condensed with the methyl group rather than the amino group of ATNT: probably the strong electron-withdrawing effect of the nitro groups decreased the nucleophilicity of the amino group. In addition, steric hindrance caused by the intra-molecular hydrogen bonds

between the amino and nitro groups also hampered the reaction progress.

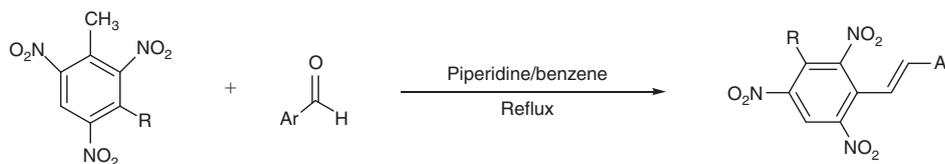
#### Thermal Stability of Polynitrostilbenes

Initially, benzaldehydes involving halogeno, methyl, and nitro substituent groups were selected to condense with TNT and ATNT. The yields of the corresponding products and their melting points are shown in Table 1, the melting points of the polynitrostilbenes with an amino group are higher than those without. The reason for the enhancement of the thermal stability may be that the amino group can facilitate the formation of inter- and intra-molecular (major) hydrogen bonds (as shown in Fig. 1) between the amino and nitro groups.

Furthermore, in order to understand the effects of the number of C=C conjugated double bonds on the thermal stability, compounds **13–15** were synthesised by the condensation of multi-substituted benzaldehydes **3A–C** with TNT and ATNT. The corresponding products and their thermal decomposition results are shown in Table 2. Compared with Table 1, the thermal stability tends to rise while increasing the number of C=C conjugated double bonds. However, the change of the thermal stability is not obvious when introducing the amino group to **13C**, which may arise from its good symmetry and dispersion between the atoms. Compounds **14** with poor symmetry show similar thermal properties to Table 1, and compounds **15** demonstrate a weaker thermal stability than compounds **13** which may be owing to the crowded position in the groups.

#### Conclusion

In summary, an efficient procedure for the preparation of new polynitrostilbenes was performed through the condensation of aromatic aldehydes with TNT and ATNT. The thermal analysis revealed that both introducing an amino group and C=C conjugated double bonds could enhance the thermal stability of the

**Table 1.** Preparation of various nitrostilbenes via reaction of aromatic benzaldehydes with 2,4,6-trinitrotoluene (TNT) and 3-amino-2,4,6-trinitrotoluene (ATNT)

Entry	Ar	Time [h]	Yield <sup>A</sup> [%]	Mp [°C]	Lit. <sup>[23]</sup> mp [°C]
1		12	73.6	194–195 <sup>B</sup>	195–196
		14	72.3	220 <sup>C</sup>	–
2		5.5	87.6	156 <sup>B</sup>	156–157
		6	91.7	232 <sup>C</sup>	–
3		9	81.2	167–168 <sup>B</sup>	165–166
		11	85.6	197 <sup>C</sup>	–
4		6	87.0	146–147 <sup>B</sup>	146–147
		7	92.1	223 <sup>C</sup>	–
5		7.5	76.4	173–175 <sup>B</sup>	–
		9	82.8	238 <sup>C</sup>	–
6		6.0	90.2	163–164 <sup>B</sup>	162–163
		6.5	93.8	229 <sup>C</sup>	–

<sup>A</sup>Isolated yield.<sup>B</sup>R = H.<sup>C</sup>R = NH<sub>2</sub>.

polynitrostilbenes. The thermal stability was also associated with the symmetry and the extent of dispersion between the atoms. The results now motivate us to further synthesise several novel polynitrostilbenes in our laboratory.

## Experimental

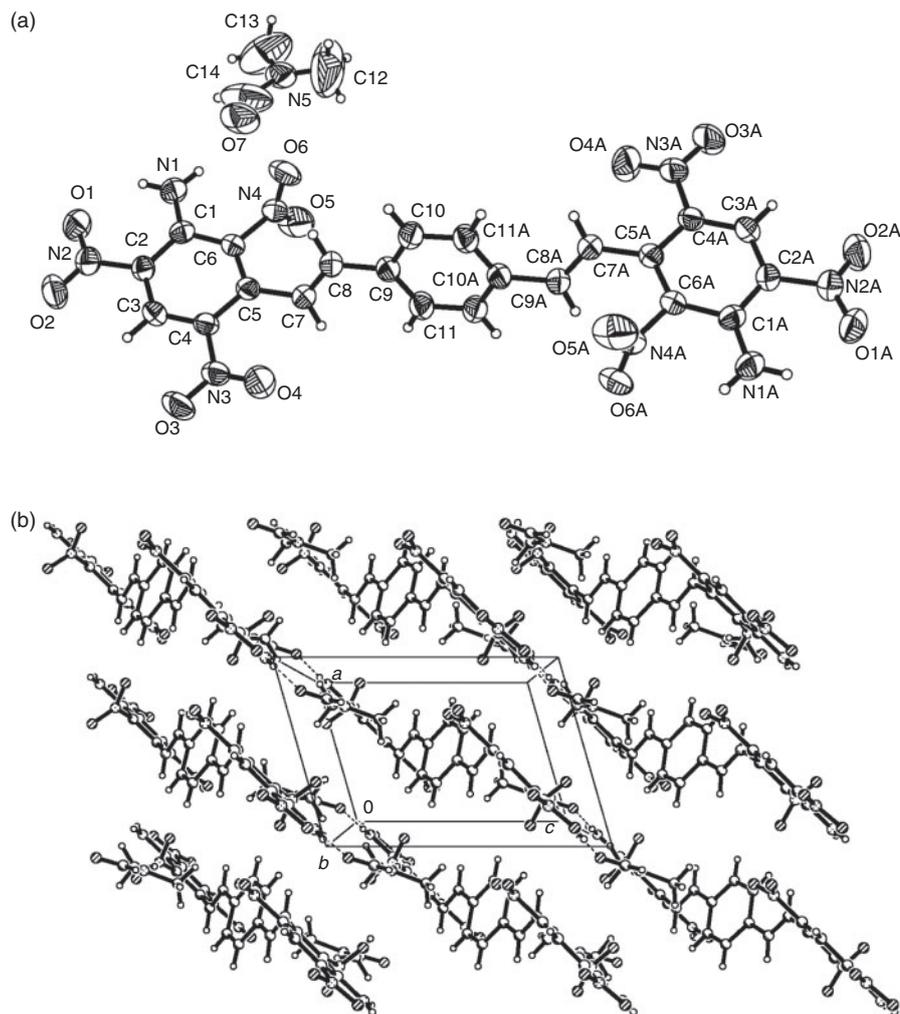
### General

All the reagents and solvents were purchased from Aladdin Chemical Company and used without further purification unless otherwise stated. All melting points were uncorrected and measured by the use of a WRS-1B digital melting point apparatus. Thermal measurements were made by using a Mettler Toledo differential scanning calorimeter. IR spectra were recorded on a FT Bruker Tensor 27 spectrometer. NMR spectra were acquired with Bruker AVANCE III 300 MHz and 500 MHz spectrometers using TMS as an internal standard.

Mass spectra were acquired with a LCQ-Advantage MS. Elemental analyses were performed on a BRUKER EURO EA.

### 1,3,5-Tris(bromomethyl)benzene (2A)

Mesitylene **1A** (10 g, 83 mmol), NBS (25 g, 140 mmol), and AIBN (70 mg, as initiator) were mixed and heated to reflux at 85°C in CCl<sub>4</sub> (100 mL) with stirring. NBS (10 g, 56 mmol) and AIBN (30 mg) were added every 1.5 h three times. After 15 h, the precipitates were removed by suction filtration and washed with CCl<sub>4</sub>. The filtrate was washed with saturated sodium hydrogen carbonate solution followed by distilled water and dried with Na<sub>2</sub>SO<sub>4</sub>. The volume was reduced to ~40 mL and then light petroleum (80 mL) was added. The solution was placed in a freezer and the resulting pellucid solution was collected. This progress was repeated several times and the solution was left to stand in the freezer overnight. The white needle crystals were then recrystallised from hexane to yield



**Fig. 1.** (a) Single crystal X-ray structure of compound **13D**, 50% thermal probability ellipsoids. A DMF solvate is shown and hydrogen atoms are omitted for clarity. (b) Ball- and stack-packing diagram of **13D** viewed down the *c*-axis. Dashed lines indicate strong hydrogen bonding.

1,3,5-tris(bromomethyl)benzene **2A** as colourless needles (3.87 g, 19.3%), mp 94–96°C (lit.<sup>[14]</sup> 87–89°C);  $R_f$  0.45 (CH<sub>2</sub>Cl<sub>2</sub>/hexane 3 : 8).  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3022w, 2969w, 1453m, 1436m, 1212s, 1163m, 1119m, 892m, 856m, 702s, 582s.  $\delta_H$  (300 MHz, CDCl<sub>3</sub>) 7.36 (3H, s, ArH), 4.45 (6H, s, CH<sub>2</sub>Br).

#### Benzene-1,3,5-tricarbaldehyde (**3A**)

Sodium methylate (2.0 g, 37.0 mmol) was dissolved in absolute methanol (60 mL), and 2-nitropropane (3.8 g, 42.7 mmol) was slowly added under intense stirring. The resulting solution was treated immediately with 1,3,5-tris(bromomethyl)benzene (**2A**) (3.0 g, 8.4 mmol) dissolved in ethyl acetate. After continuously stirring at 30°C for 6 h, distilled water (30 mL) and ethyl acetate (40 mL) were added, and the solution was allowed to stand overnight and extracted with ethyl acetate (4 × 30 mL). The combined organic extracts were washed with 10% sodium hydroxide aqueous solution, 10% hydrochloric acid, saturated sodium bicarbonate solution, and dried with Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent, the solid was washed with diethyl ether to yield benzene-1,3,5-tricarbaldehyde (**3A**) as white crystals (1.1 g, 80.8%), mp 159–160°C (lit.<sup>[15]</sup> 149–150°C).  $R_f$  0.4 (EtOAc/hexane 1 : 5).  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3058m, 2744w,

1696s, 1592s, 1448s, 1137s, 962s, 888m, 648s.  $\delta_H$  (300 MHz, CDCl<sub>3</sub>) 10.20 (3H, s, CHO), 8.64 (3H, s, ArH).

#### Terephthalaldehyde (**3B**)

Following the above mentioned procedure, the product **3B** was obtained as white needle crystals, yield 23.6%, mp 246–248°C.  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 2755m, 1692s, 1496m, 1197s, 814s.  $\delta_H$  (300 MHz, CDCl<sub>3</sub>) 10.15 (2H, s, CHO), 8.07 (4H, s, ArH).

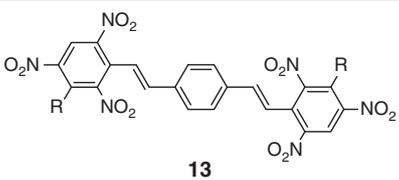
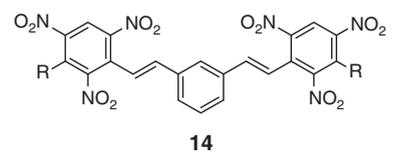
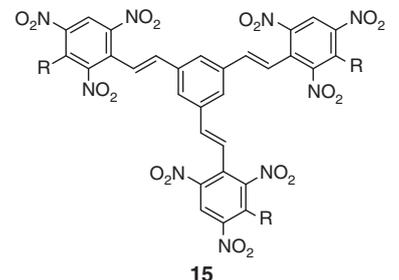
#### Isophthalaldehyde (**3C**)

Yield: 25.8%, mp 88–90°C; white crystals.  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 2757m, 1694s, 1596m, 1137s, 795s.  $\delta_H$  (300 MHz, CDCl<sub>3</sub>) 10.11 (2H, s, CHO), 8.37 (1H, s, ArH), 8.17 (2H, d, *J* 9, ArH), 7.76 (1H, dd, *J*<sub>1</sub> 7.5, *J*<sub>2</sub> 7.5, ArH).

#### ATNT (**6**)

The preparation of *N*-(3-methylphenyl)ethylcarbamate (**5**) was previously reported in the literature.<sup>[16,21]</sup> To a solution of sulfuric acid (4.60 g, 46.9 mmol) and fuming nitric acid (0.81 g, 12.7 mmol) was added dropwise *N*-(3-methylphenyl)ethylcarbamate (**5**) (0.50 g, 2.8 mmol) at 25°C with stirring during 0.5 h followed by adding glycol–water (15 mL–5 mL), keeping

**Table 2.** Preparation and thermal property of polynitrostilbenes with two or three C=C double bonds

Entry	Polynitrostilbenes	Time [h]	Yield <sup>A</sup> [%]	Initial decomp. <sup>B</sup> [°C]	Peak <sup>B</sup> [°C]
1	 <b>13</b>	12	95.1	299.78	301.13 <sup>C</sup>
		11	93.2	298.70	300.69 <sup>D</sup>
2	 <b>14</b>	11	89.5	252.73	256.87 <sup>C</sup>
		11	95.7	272.09	282.51 <sup>D</sup>
3	 <b>15</b>	14	90.3	262.14	309.49 <sup>C</sup>
		16	96.0	274.43	285.60 <sup>D</sup>

<sup>A</sup>Isolated yield.<sup>B</sup>Differential scanning calorimetry, heating rate 5°C min<sup>-1</sup>.<sup>C</sup>R = H.<sup>D</sup>R = NH<sub>2</sub>.

the temperature below 40°C. The mixture was then heated to 95°C and maintained for ~7 h. After completion as determined by TLC, the mixture was poured into 200 mL of water to form a yellow precipitate which was then filtered off, washed, and dried to yield ATNT **6** (0.58 g, 85.9%), mp 138°C (lit.<sup>[21]</sup> 135–136°C, lit.<sup>[22]</sup> 138–138.5°C). *R<sub>f</sub>* 0.52 (EtOAc/hexane, 1 : 5).  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>) 9.11 (1H, s, ArH), 2.63 (3H, s, CH<sub>3</sub>).

*(E)*-3-Amino-4'-nitro-2,4,6-trinitrostilbene (**7C**)

4-Nitrobenzaldehyde (0.33 g, 2.2 mmol), ATNT (**6**) (0.5 g, 2.1 mmol), benzene (40 mL), and piperidine (0.085 g, 1.0 mmol) were placed in a 50 mL flask fitted with a Dean–Stark trap. The mixture was refluxed till completion as determined by TLC. After evaporation of benzene (30 mL), ethanol was added dropwise to the residue until a precipitate appeared. The mixture was then cooled and placed in a freezer overnight. The product was collected, washed, and dried to yield 3-amino-4'-nitro-2,4,6-trinitrostilbene (**7C**) as yellow crystals (0.57 g, 72.3%), mp 220°C. *R<sub>f</sub>* 0.3 (EtOAc/hexane, 1 : 3).  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 3463m, 3335m, 1616s, 1537s, 1505s, 1425m, 1340s, 958w, 823m.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>) 9.25 (1H, s, ArH), 8.28 (2H, d, *J* 9, ArH), 7.64 (2H, d, *J* 8.5, ArH), 7.54 (1H, d, *J* 16.5, vinylic CH), 6.70 (1H, d, *J* 16.5, vinylic CH). *m/z* (ESI) 374 [M – H]<sup>-</sup>. Anal. Calc. for C<sub>14</sub>H<sub>9</sub>N<sub>5</sub>O<sub>8</sub> (375.05): C 44.81, H 2.42, N 18.66. Found: C 44.76, H 2.26, N 18.61%.

*(E)*-3-Amino-4'-chloro-2,4,6-trinitrostilbene (**8C**)

Following a procedure similar to that of **7C**, the product was obtained as yellow crystals, yield 91.7%, mp 232°C.  $\nu_{\text{max}}$

(KBr)/cm<sup>-1</sup> 3456s, 3352s, 1623s, 1580s, 1543s, 1493s, 1342s, 1276s, 972m, 814m, 702w.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>) 9.20 (1H, s, ArH), 7.42 (2H, d, *J* 9, ArH), 7.38 (2H, d, *J* 9, ArH), 7.36 (1H, d, *J* 16.5, vinylic CH), 6.64 (1H, d, *J* 16.5, vinylic CH). *m/z* (ESI) 363 [M – H]<sup>-</sup>. Anal. Calc. for C<sub>14</sub>H<sub>9</sub>ClN<sub>4</sub>O<sub>6</sub> (364.02): C 46.11, H 2.49, N 15.36. Found: C 46.05, H 2.36, N 15.30%.

*(E)*-3-Amino-2',4'-dichloro-2,4,6-trinitrostilbene (**9C**)

Yield: 85.6%, mp 197°C, yellow crystals.  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 3458m, 3353s, 1621s, 1578s, 1543s, 1332s, 1278s, 970w, 893w, 816w, 707w.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>) 9.22 (1H, s, ArH), 7.55 (1H, d, *J* 2.5, ArH), 7.48 (1H, d, *J* 8.5, ArH), 7.37 (1H, d, *J* 16.5, vinylic CH), 7.32 (1H, dd, *J*<sub>1</sub> 8.5, *J*<sub>2</sub> 2.0, ArH), 6.57 (1H, d, *J* 16.5, vinylic CH). *m/z* (ESI) 397 [M – H]<sup>-</sup>. Anal. Calc. for C<sub>14</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>6</sub> (397.98): C 42.13, H 2.02, N 14.04. Found: C 42.10, H 1.94, N 14.02%.

*(E)*-3-Amino-2'-chloro-2,4,6-trinitrostilbene (**10C**)

Yield: 92.1%, mp 223°C, yellow needles.  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 3452s, 3344s, 1623s, 1579s, 1538s, 1512s, 1362m, 1327s, 974m, 771m, 698m.  $\delta_{\text{H}}$  (500 Hz, CDCl<sub>3</sub>) 9.24 (1H, s, ArH), 7.71 (1H, dd, *J*<sub>1</sub> 7, *J*<sub>2</sub> 2, ArH), 7.42 (1H, dd, *J*<sub>1</sub> 7.5, *J*<sub>2</sub> 1.5, ArH), 7.39 (3H, m), 7.09 (1H, d, *J* 16.5, vinylic CH). *m/z* (ESI) 363 [M – H]<sup>-</sup>. Anal. Calc. for C<sub>14</sub>H<sub>9</sub>ClN<sub>4</sub>O<sub>6</sub> (364.02): C 46.11, H 2.49, N 15.36. Found: C 46.07, H 2.42, N 15.32%.

*(E)*-4'-Bromo-2,4,6-trinitrostilbene (**11B**)

Yield: 76.4%, mp 173–175°C, yellow crystals.  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup> 3087s, 1632m, 1597s, 1541s, 1486s, 1400m, 1347s, 973m,

817s, 516m.  $\delta_{\text{H}}$  (300MHz,  $\text{CDCl}_3$ ) 8.90 (2H, s, ArH), 7.57 (2H, d,  $J$  8.4, ArH), 7.38 (3H, dd,  $J_1$  8.4,  $J_2$  7.8 Hz), 6.74 (2H, d,  $J$  16.8, vinylic CH).  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ) 150.11, 145.99, 137.34, 133.58, 133.45, 132.15, 128.79, 124.30, 122.21, 117.12. Anal. Calc. for  $\text{C}_{14}\text{H}_8\text{BrN}_3\text{O}_6$  (392.96): C 42.66, H 2.05, N 10.66. Found: C 42.62, H 1.91, N 10.57%.

(E)-3-Amino-4'-bromo-2,4,6-trinitrostilbene (**11C**)

Yield: 82.8%, mp 238°C, yellow crystals.  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3456s, 3351s, 1622s, 1579s, 1543s, 1528s, 1491m, 1341s, 1276s, 974m, 812m, 493w.  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 9.20 (1H, s, ArH), 7.54 (2H, d,  $J$  8.5, ArH), 7.37 (3H, m), 6.62 (1H, d,  $J$  16.5, vinylic CH).  $m/z$  (ESI) 407 [M-H]<sup>-</sup>. Anal. Calc. for  $\text{C}_{14}\text{H}_9\text{BrN}_4\text{O}_6$  (407.97): C 41.10, H 2.22, N 13.69. Found: C 41.07, H 2.10, N 13.61%.

(E)-3-Amino-4'-methyl-2,4,6-trinitrostilbene (**12C**)

Yield: 93.8%; mp 229°C; orange crystals.  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3456s, 3351s, 1621s, 1578s, 1543s, 1428m, 1339s, 1280s, 979m, 808m.  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 9.18 (1H, s, ArH), 7.38 (2H, d,  $J$  8.5, ArH), 7.33 (1H, d,  $J$  16.5, vinylic CH), 7.21 (2H, d,  $J$  8.0, ArH), 6.69 (1H, d,  $J$  16.5, vinylic CH), 2.385 (3H, s,  $\text{CH}_3$ ).  $m/z$  (ESI) 343 [M-H]<sup>-</sup>. Anal. Calc. for  $\text{C}_{15}\text{H}_{12}\text{N}_4\text{O}_6$  (344.08): C 52.33, H 3.51, N 16.27. Found: C 52.30, H 3.44, N 16.24%.

1,4-Bis(2,4,6-trinitrostyryl)benzene<sup>[5]</sup> (**13C**)

Yield: 95.1%, yellow crystals.  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3085s, 1598s, 1566s, 1504s, 1367s, 1315s, 1198m, 970s, 812s.  $\delta_{\text{H}}$  (300 MHz,  $\text{DMSO}-d_6$ ) 9.12 (4H, s, ArH), 7.66 (4H, s, ArH), 7.59 (2H, d,  $J$  16.5, vinylic CH), 6.85 (2H, d,  $J$  16.5, vinylic CH). Anal. Calc. for  $\text{C}_{22}\text{H}_{12}\text{N}_6\text{O}_{12}$  (552.05): C 47.84, H 2.19, N 15.21. Found: C 47.80, H 2.12, N 15.15%.

3,3'-(1E,1'E)-2,2'-(1,4-Phenylene)bis(ethane-2,1-diy)bis(2,4,6-trinitroaniline) (**13D**)

Yield: 93.2%, orange crystals.  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3480m, 3361s, 1614s, 1571s, 1536s, 1508s, 1328s, 1284s, 977m, 813m.  $\delta_{\text{H}}$  (300 MHz,  $\text{DMSO}-d_6$ ) 8.96 (2H, s, ArH), 8.41 (4H, s,  $\text{NH}_2$ ), 7.62 (4H, s, ArH), 7.50 (2H, d,  $J$  16.5, vinylic CH), 6.74 (2H, d,  $J$  16.5, vinylic CH).  $\delta_{\text{C}}$  (75 MHz,  $\text{DMSO}-d_6$ ) 140.89, 139.66, 136.44, 134.34, 134.09, 133.79, 130.68, 128.01, 126.27, 120.95.  $m/z$  (ESI) 580.82 [M-H]<sup>-</sup>. Anal. Calc. for  $\text{C}_{22}\text{H}_{14}\text{N}_8\text{O}_{12}$  (582.07): C 45.37, H 2.42, N 19.24. Found: C 45.33, H 2.37, N 19.23%.

1,3-Bis(2,4,6-trinitrostyryl)benzene<sup>[5]</sup> (**14C**)

Yield: 89.5%, mp 241.5°C, yellow crystals.  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3080m, 1602s, 1534s, 1403m, 1346s, 917m, 798m, 725m.  $\delta_{\text{H}}$  (300 MHz,  $\text{DMSO}-d_6$ ) 9.14 (4H, s, ArH), 7.84 (1H, s, ArH), 7.66 (3H, dd,  $J_1$  7.5,  $J_2$  3.9, ArH), 7.57 (2H, d,  $J$  16.8, vinylic CH), 6.88 (2H, d,  $J$  16.8, vinylic CH). Anal. Calc. for  $\text{C}_{22}\text{H}_{12}\text{N}_6\text{O}_{12}$  (552.05): C 47.84, H 2.19, N 15.21. Found: C 47.81, H 2.12, N 15.18%.

3,3'-(1E,1'E)-2,2'-(1,3-Phenylene bis(ethene-2,1-diy) bis(2,4,6-trinitroaniline) (**14D**)

Yield: 95.7%, mp 272°C, orange solid.  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3446m, 3345s, 1619s, 1578s, 1536s, 1429m, 1332s, 1283s, 964w, 793m.  $\delta_{\text{H}}$  (300 MHz,  $\text{DMSO}-d_6$ ) 8.97 (2H, s, ArH), 8.42 (4H, s,  $\text{NH}_2$ ), 7.77 (1H, s, ArH), 7.60 (2H, d,  $J$  7.5, ArH), 7.54 (3H, m), 6.75 (2H, d,  $J$  16.5, vinylic CH).  $\delta_{\text{C}}$  (75 MHz,

$\text{DMSO}-d_6$ ) 140.88, 139.67, 136.31, 134.31, 134.09, 133.90, 130.71, 129.94, 128.10, 126.28, 126.02, 120.98.  $m/z$  (ESI) 580.89 [M-H]<sup>-</sup>. Anal. Calc. for  $\text{C}_{22}\text{H}_{14}\text{N}_8\text{O}_{12}$  (582.07): C 45.37, H 2.42, N 19.24. Found: C 45.30, H 2.32, N 19.21%.

1,3,5-Tris(2,4,6-trinitrostyryl)benzene<sup>[5]</sup> (**15C**)

Yield: 90.3%, yellow crystals.  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3094s, 1606s, 1564s, 1515s, 1346s, 1174m, 970s, 918s.  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ) 8.97 (6H, s, ArH), 7.57 (3H, s, ArH), 7.50 (3H, d,  $J$  17.4, vinylic CH), 6.82 (3H, d,  $J$  17.4, vinylic CH); Anal. Calc. for  $\text{C}_{30}\text{H}_{15}\text{N}_6\text{O}_{18}$  (789.05): C 45.64, H 1.92, N 15.97. Found: C 45.60, H 1.81, N 15.94%.

3,3',3''-(1E,1'E,1''E)-2,2',2''-(Benzene-1,3,5-triyl)tris(ethene-2,1-diy)tris(2,4,6-trinitroaniline) (**15D**)

Yield: 96%, orange solid.  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3464m, 3359s, 1624s, 1579s, 1526s, 1333s, 1284s, 966m, 893w.  $\delta_{\text{H}}$  (300 MHz,  $\text{DMSO}-d_6$ ) 8.95 (3H, s, ArH), 8.41 (6H, s,  $\text{NH}_2$ ), 7.78 (3H, s, ArH), 7.62 (3H, d,  $J$  16.5, vinylic CH), 6.75 (3H, d,  $J$  16.5, vinylic CH).  $\delta_{\text{C}}$  (75 MHz,  $\text{DMSO}-d_6$ ) 140.92, 139.66, 136.95, 134.18, 134.09, 130.80, 128.68, 126.46, 126.34, 121.72.  $m/z$  (ESI) 832.69 [M-H]<sup>-</sup>. Anal. Calc. for  $\text{C}_{30}\text{H}_{18}\text{N}_{12}\text{O}_{18}$  (834.09): C 43.18, H 2.17, N 20.14. Found: C 43.12, H 2.09, N 20.10%.

X-Ray Crystallographic Analysis of **13D**

Orange crystals of  $\text{C}_{22}\text{H}_{14}\text{N}_8\text{O}_{12}$  with wavelength of 0.71073,  $P2_1/c$ ,  $a$  6.608(2) Å,  $b$  27.208(9) Å,  $c$  9.503(3) Å,  $V$  1644.1 (9) Å<sup>3</sup>,  $Z$  2,  $D_x$  1.472 g cm<sup>-3</sup>. Correction method was MULTISCAN, final  $R$  indicates  $R_1$  0.0642,  $wR_2$  0.1590. Crystallographic data for **13D** have been deposited in the Cambridge Crystallographic Data Centre with the deposition number 1004138. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033, email: deposit@ccdc.cam.ac.uk).

Supplementary Material

<sup>1</sup>H and <sup>13</sup>C NMR, mass spectrometry, and differential scanning calorimetry spectra are available on the Journal's website.

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