

# Square networks based on the Br...NO<sub>2</sub> supramolecular synthon\*

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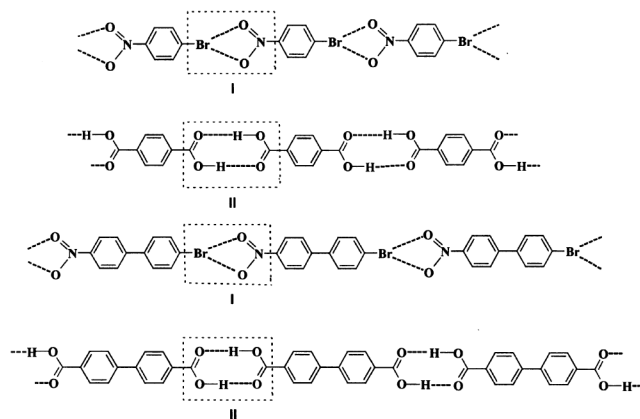
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Six polysubstituted bromonitrobenzenes have been prepared by nitration of the three isomeric dibromobenzenes and their crystal structures analysed in terms of network architectures. The dominant intermolecular interactions in these structures are the polarization-induced Br...NO<sub>2</sub> and the C–H...O bridges that are promoted by the activation of the C–H groups in these electron-deficient systems. The Br...NO<sub>2</sub> interactions act as one-dimensional connectors and, in this sense, may be termed as supramolecular synthons. A networking of these polyfunctional molecules leads to two-dimensional square and hexagonal networks. In one favourable case, the overall crystal packing is in a non-centrosymmetric space group and the alignment of chromophores leads to significant SHG properties. Even for small, simple molecules of the type studied here, crystal structure prediction is difficult and no two compounds have exactly the same crystal structure.

THE network depiction of a crystal structure is an advantageous concept in crystal engineering<sup>1</sup>. In this topological strategy, crystal structures are defined as networks with nodes and node connections. Typically, atoms, ions or molecules are considered as nodes and intermolecular interactions or coordination bonds are taken as node connections. Alternatively, both molecules and supramolecular synthons<sup>2</sup> may be taken as nodes, and the node connections become mere abstractions. Targeting a network rather than a complete crystal structure assumes structural modularity and reduces the levels of complexity in crystal engineering. One, two, or three-dimensional crystalline networks may be engineered by choosing a desired combination of nodes and node connections. This approach is favoured in the study of coordination polymers<sup>3</sup> but it may also be employed in crystal engineering of pure organics. There are several reports on the design of ladder, brick wall, herringbone and honeycomb networks in

organic structures using T-shaped molecules<sup>4</sup>. However, square grid networks which are ubiquitous among coordination polymers are not so common among organic structures, there being only a few reports on pyromellitic acid and its derivatives. This paper describes square grid networks in a group of bromonitrobenzenes.

Among compounds that contain bromo and nitro groups, the Br...NO<sub>2</sub> synthon I is common<sup>5</sup>. This one-dimensional synthon has some similarity to the carboxyl dimer synthon, II. Synthons I and II can act as connectors of bifunctional molecules to form one-dimensional patterns. Accordingly, 4-bromonitrobenzene and terephthalic acid have similar tape motifs in the solid state, and similarities are also observed in the corresponding 4,4'-disubstituted biphenyls (Scheme 1)<sup>6</sup>. With such interchangeability of synthons in one-dimensional systems possible, we were hopeful that this idea could be extended to two-dimensional patterns. It is known that pyromellitic acid (benzene-1,2,4,5-tetracarboxylic acid) forms a square grid network<sup>7</sup>. Would such networks also be possible in appropriately polysubstituted bromonitrobenzenes? For example, would square networks based on synthon I be found in the crystal structures of the three isomeric 1,2,4,5-tetrasubstituted dibromodinitrobenzenes (1–3) as shown in Scheme 2?



**Scheme 1.** Similarity between Br...NO<sub>2</sub> synthon, I, and carboxyl dimer synthon, II.

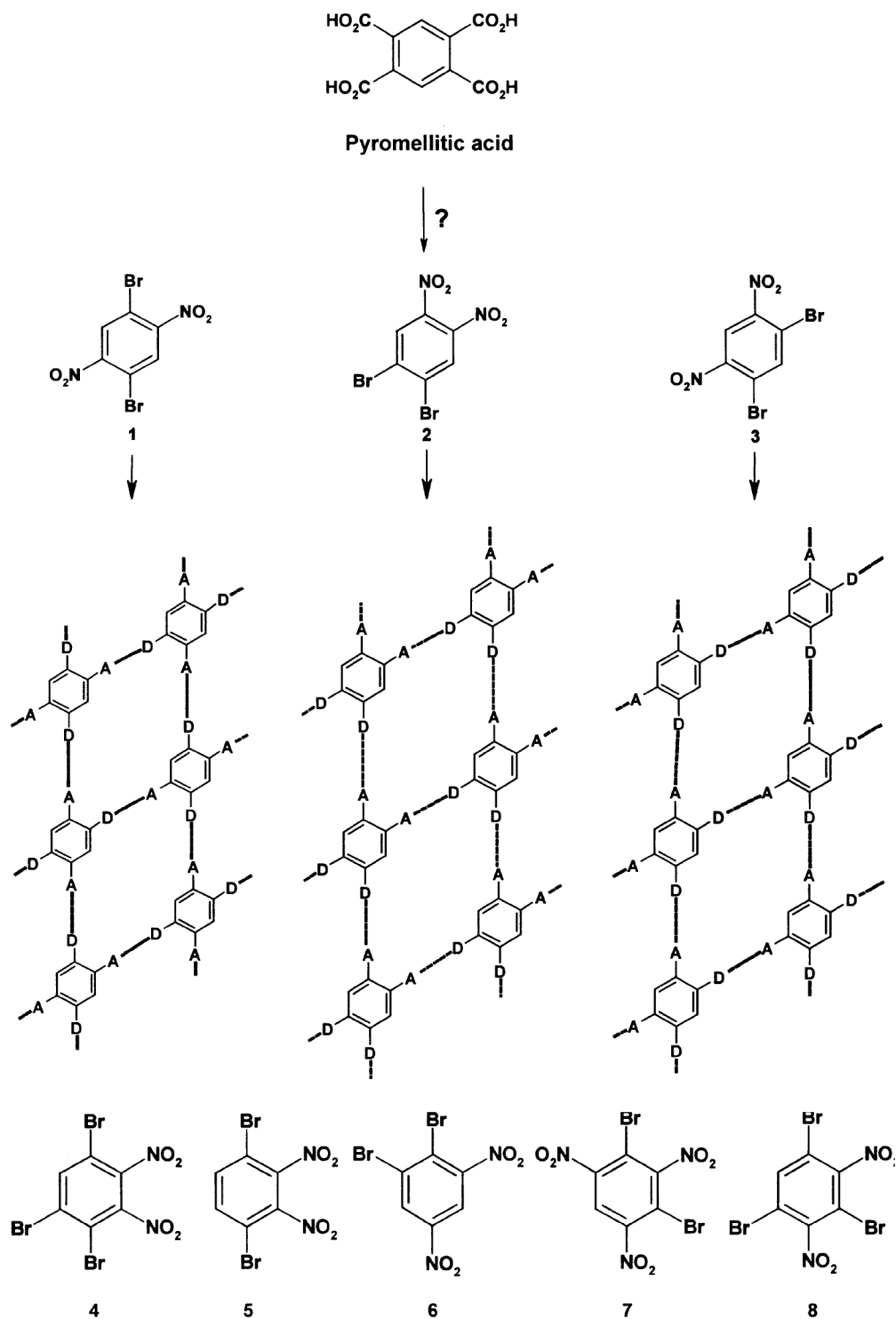
\*Dedicated to Prof. S. Ramaseshan on his 80th birthday.

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## Experimental

With this background on synthon interchangeability, we attempted to prepare compounds 1–3 via nitration of the appropriate dibromobenzene. Typically, a large number of nitrated products were obtained in each case and sepa-

ration by column chromatography (silica gel, hexane) was necessary. We could not isolate compounds 1 and 2 in tangible amounts but we could separate compound 3. Another five derivatives 4 through 8 were obtained. We have reported the crystal structure of compound 7 earlier<sup>8</sup>. In this paper, we describe the crystal structures of the



**Scheme 2.** Three isomeric dibromodinitrobenzenes based on pyromellitic acid and putative network structures based on the Br...NO<sub>2</sub> synthon, I (D = Br and A = NO<sub>2</sub>).

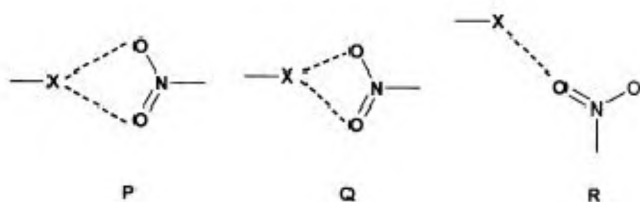
**Table 1.** Crystallographic details for the compounds in this study

	3	4	5	6	8
Chemical formula	C <sub>6</sub> H <sub>2</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	C <sub>6</sub> HBr <sub>3</sub> N <sub>2</sub> O <sub>4</sub>	C <sub>6</sub> H <sub>2</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	C <sub>6</sub> H <sub>2</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	C <sub>6</sub> HBr <sub>3</sub> N <sub>2</sub> O <sub>4</sub>
Formula weight	325.9	404.8	325.9	325.9	404.8
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> -1	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	14.370(7)	7.875(8)	17.00(1)	8.789(6)	6.745(3)
<i>b</i> (Å)	9.731(2)	8.021(8)	7.682(6)	15.47(1)	9.825(5)
<i>c</i> (Å)	20.261(9)	9.169(9)	7.955(4)	13.451(6)	16.267(7)
$\alpha$ (°)	90	70.07(2)	90	90	90
$\beta$ (°)	98.32(1)	84.63(2)	116.13(4)	90.50(3)	98.95(3)
$\gamma$ (°)	90	66.36(2)	90	90	90
<i>V</i>	2803.4(2)	498.2(9)	932.8(1)	1829.9(2)	1064.9(8)
<i>Z</i>	12	2	4	8	4
<i>R</i> <sub>1</sub>	0.060	0.0882	0.045	0.050	0.047
<i>W</i> <sub>R</sub> <sub>2</sub>	0.074	0.0953	0.051	0.056	0.047
CCDC	217344	217345	217346	217347	217348

polybromonitrobenzenes that are given in Table 1. Except for compound **4**, single crystal X-ray data were collected on a Nonius-CCD Kappa diffractometer working with AgK $\alpha$  radiation. Absorption correction was applied for the Br atoms. Hydrogen atoms were refined in such a way that the ratio of reflections to parameters for each crystal structures is favourable ( $\sim 10$ ). Structures were solved using direct methods with SIR92 program<sup>9</sup>. Full-matrix least-squares refinement was performed on *F* using the teXsan software<sup>10</sup>. Scattering factors for neutral atoms and *f'*,  $\Delta f'$ , *f''*,  $\Delta f''$  were taken from *International Tables for X-ray Crystallography*<sup>11</sup>. Single crystal X-ray data for **4** was collected using Siemens X-ray diffractometer<sup>12</sup>. SHELXS and SHELXL were used for the solution and refinement<sup>13</sup>. Details of crystal data are listed in Table 1 and metrics of some important hydrogen bonds are summarized in Table 2.

## Results and discussion

As discussed previously in a paper from the Hyderabad group, X $\cdots$ O<sub>2</sub>N contacts are of three types<sup>14</sup>: a bifurcated contact where both the distances are equal ( $D_1 \cong D_2$ ), a more unsymmetrical contact where  $D_1 > D_2$  and finally a contact where only one of the two nitro group O-atoms makes a contact with atom X. These three types of contacts, denoted by **P**, **Q** and **R**, are shown in Scheme 3. Generally, the proportion of **P** contacts decreases as one proceeds from Cl  $\rightarrow$  Br  $\rightarrow$  I. These trends have been generally noted in subsequent studies.

**Scheme 3.** Three types of Br $\cdots$ NO<sub>2</sub> interactions.

### 1,5-dibromo-2,4-dinitrobenzene, **3**

Compound **3** was prepared according to the literature procedure<sup>15</sup>. Single crystals of **3**, suitable for X-ray diffraction studies were grown from acetic acid. The compound crystallizes in the centrosymmetric space group

**Table 2.** Pertinent intermolecular interactions in compounds **3–8**

Structure	Interaction	<i>d</i> (Å)	$\theta$ (°)
<b>3</b>	C–H $\cdots$ O	2.83	159.7
	C–H $\cdots$ O	2.58	163.6
	C–H $\cdots$ O	2.46	175.6
	Br $\cdots$ NO <sub>2</sub>	3.17	164.2
	Br $\cdots$ NO <sub>2</sub>	3.44	150.9
	Br $\cdots$ NO <sub>2</sub>	3.02	170.0
	Br $\cdots$ NO <sub>2</sub>	3.45	129.1
	Br $\cdots$ NO <sub>2</sub>	3.20	154.7
	Br $\cdots$ NO <sub>2</sub>	3.22	153.2
	Br $\cdots$ NO <sub>2</sub>	3.45	129.1
<b>4</b>	C–H $\cdots$ O	2.45	156.2
	Br $\cdots$ NO <sub>2</sub>	3.16	168.6
	Br $\cdots$ NO <sub>2</sub>	3.22	169.3
	Br $\cdots$ NO <sub>2</sub>	3.44	130.9
	Br $\cdots$ Br	3.92	72.8; 92.4
	Br $\cdots$ Br	3.55	128.0; 124.9
<b>5</b>	C–H $\cdots$ O	2.72	138.3
	Br $\cdots$ NO <sub>2</sub>	3.45	143.5
	Br $\cdots$ NO <sub>2</sub>	3.15	160.9
<b>6</b>	C–H $\cdots$ O	2.62	151.6
	C–H $\cdots$ O	2.67	147.8
	Br $\cdots$ NO <sub>2</sub>	3.45	120.2
	Br $\cdots$ Br	3.72	118.4; 173.5
	Br $\cdots$ Br	3.72	161.7; 122.7
<b>7</b>	C–H $\cdots$ O	2.66	155.2
	Br $\cdots$ NO <sub>2</sub>	2.93	169.0
	Br $\cdots$ NO <sub>2</sub>	3.48	155.0
<b>8</b>	C–H $\cdots$ O	2.94	159.1
	Br $\cdots$ NO <sub>2</sub>	3.31	150.2
	Br $\cdots$ NO <sub>2</sub>	3.35	145.0
	Br $\cdots$ NO <sub>2</sub>	3.28	160.1
	Br $\cdots$ Br	3.76	109.1

$P2_1/n$  with three symmetry independent molecules in the asymmetric unit. The crystal structure analysis reveals the formation of layers within which are arranged all the molecules in a square network fashion. A closer inspection of the structure shows that there are two independent square networks generated from three crystallographically symmetry independent molecules. One of the symmetry independent molecules forms a square network structure as shown in Figure 1 *a*. Figure 1 *b* shows another square network structure formed by the two remaining symmetry independent molecules. The square grid in Figure 1 *a* is made up of only **R**-type  $\text{Br}\cdots\text{NO}_2$  interactions whereas the square grid in Figure 1 *b* is generated by a combination of **Q** and **R**-type interactions. Each square grid in Figure 1 *a* and *b* is additionally stabilized by  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds<sup>16</sup>. To complete the structure these two square networks are connected by additional  $\text{Br}\cdots\text{O}_2\text{N}$  interactions (Table 2).

#### 1,2,5-tribromo-3,4-dinitrobenzene, 4

Compounds **4** and **5** were isolated as major products in the nitration of 1,4-dibromobenzene. Single crystals of **4** suitable for X-ray diffraction were grown from acetic acid. The crystal belongs to the centrosymmetric space group  $P-1$  with one molecule in the asymmetric unit. The crystal

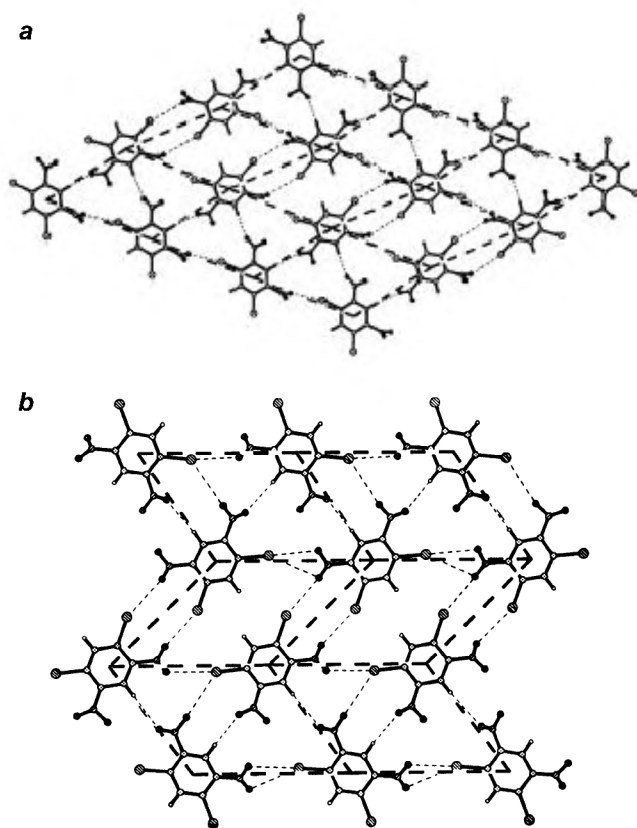


Figure 1. Two independent square networks in **3**.

structure shows the formation of a nearly perfect layer structure parallel to the (200) planes within which all molecules are arranged in a hexagonal fashion as shown in Figure 2 *a*. All the molecules in the hexagonal network are arranged in a head-to-tail fashion and are connected by  $\text{Br}\cdots\text{NO}_2$  and  $\text{C}-\text{H}\cdots\text{O}$  interactions. The bold lines in Figure 2 *b* represent the square grid network and each square grid is made up of four molecules of **4**, linked by  $\text{Br}\cdots\text{NO}_2$  **R**-type interactions. Each square grid is in turn connected by  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bridges as before<sup>17</sup>. To complete the structure, the inversion-related layers are connected by additional weak  $\text{C}-\text{H}\cdots\text{O}$  bridges.

#### 1,4-dibromo-2,3-dinitrobenzene, 5

Compound **5** takes the centrosymmetric space group  $C2/c$  with a half molecule in the asymmetric unit. The layered structure is parallel to the (002) planes and all the molecules are again arranged in a hexagonal fashion (Figure 3 *a*). The hexagonal networks are made up of  $\text{Br}\cdots\text{NO}_2$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bridges. Like **4**, structure **5** may also be analysed in terms of a square network (bold lines in Figure 3 *b*). Each square grid is made up of **R**-type  $\text{Br}\cdots\text{NO}_2$  interactions and is interlinked by  $\text{C}-\text{H}\cdots\text{O}$  bridges.

#### 1,2-dibromo-3,5-dinitrobenzene, 6

Compound **6**, adopts the centrosymmetric space group  $P2_1/c$  with one molecule in the asymmetric unit. Both the

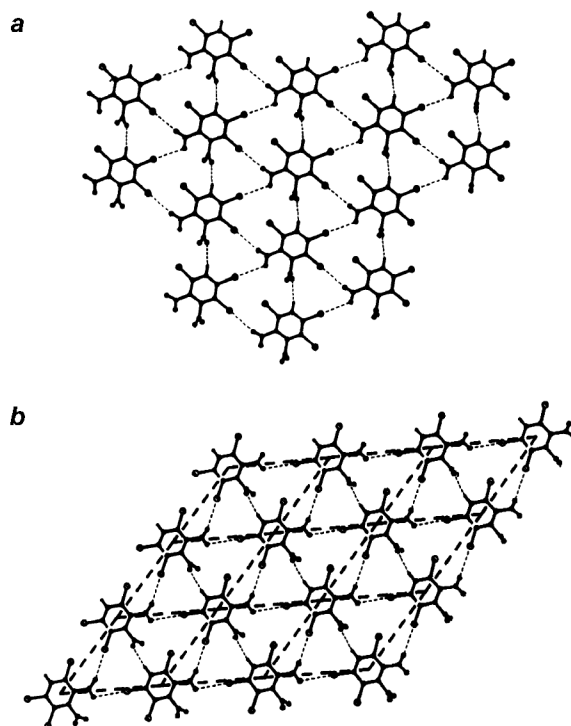


Figure 2. Hexagonal and square networks in structure **4**.

nitro groups in the molecule are out-of-plane and the overall non-planarity of the molecule generates a corrugated 2D motif. Possibly it is this corrugation that leads to centrosymmetry (Figure 4). A closer look at the corru-

gated layers shows zigzag tapes generated alternately from synthons **III** and **IV**. These tapes are connected by **R**-type  $\text{Br}\cdots\text{NO}_2$  interactions and the layers with  $\text{Br}\cdots\text{NO}_2$ ,  $\text{Br}\cdots\text{Br}$  and  $\text{C-H}\cdots\text{O}$  interactions (Figure 5).

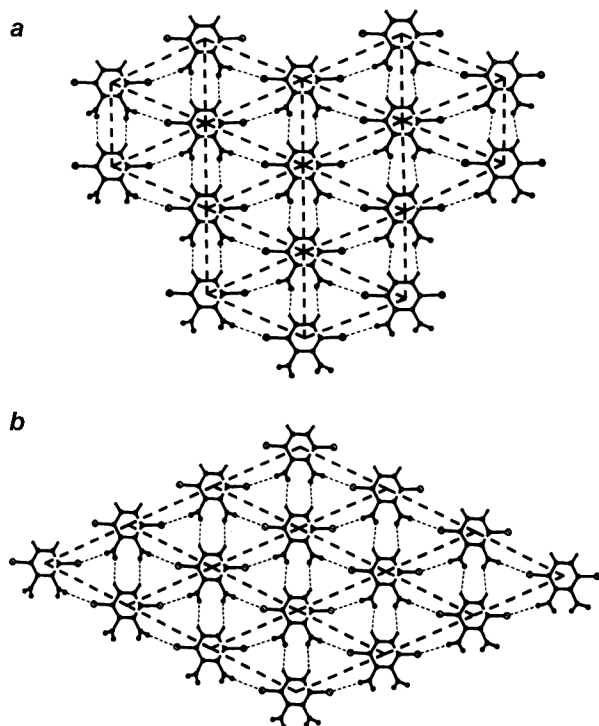


Figure 3. Hexagonal and square networks in compound 5.

### 1,3,5-tribromo-2,4-dinitrobenzene, **8**

The crystal structure of 1,3-dibromo-2,4,6-trinitrobenzene **7** and its NLO properties have been described earlier<sup>8</sup>. There is a hexagonal arrangement of molecules assembled with bifurcated  $\text{C-H}\cdots\text{O}$  and **R**-type  $\text{Br}\cdots\text{NO}_2$  interactions (Figure 6). A consequence of this perfect alignment of chromophores (and the non-centrosymmetric space group) is that the SHG of the title compound is 15 times more than that of urea.

With this background we examined the related 1,3,5-tribromo-2,4-dinitrobenzene, **8**. However, **8**, crystallizes in a centrosymmetric space group ( $P2_1/n$ ,  $Z' = 1$ ). The crystal packing of **8** is also quite different from that of **7**. Figure 7 shows a corrugated layer in which all the molecules are arranged in a hexagonal fashion and connected with  $\text{Br}\cdots\text{NO}_2$  interactions. It is possible that the reduced activation of the  $\text{C-H}$  groups leads to the lesser likelihood of  $\text{C-H}\cdots\text{Br}$  interactions, and this in turn along with the out-of-plane nature of the two nitro groups could lead to the formation of the centrosymmetric corrugated layer structure. In compound **7**, in contrast, the enhanced acidity of the  $\text{C-H}$  group and the roles of the in-plane nitro

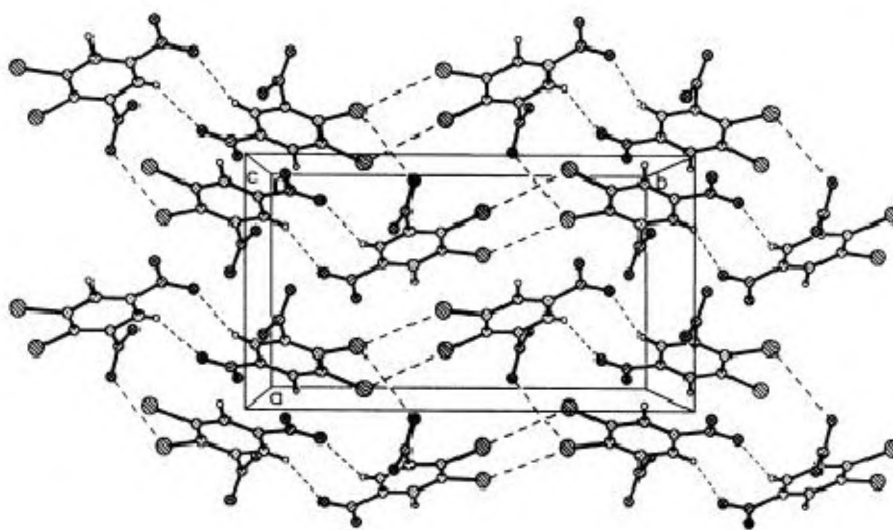
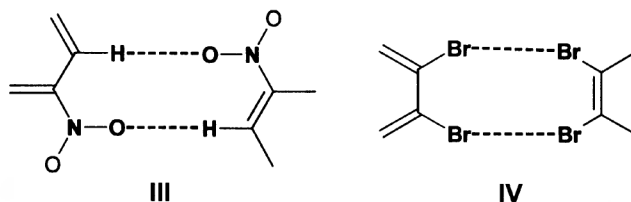


Figure 4. Corrugated layer in **6**. Notice the zigzag tapes.

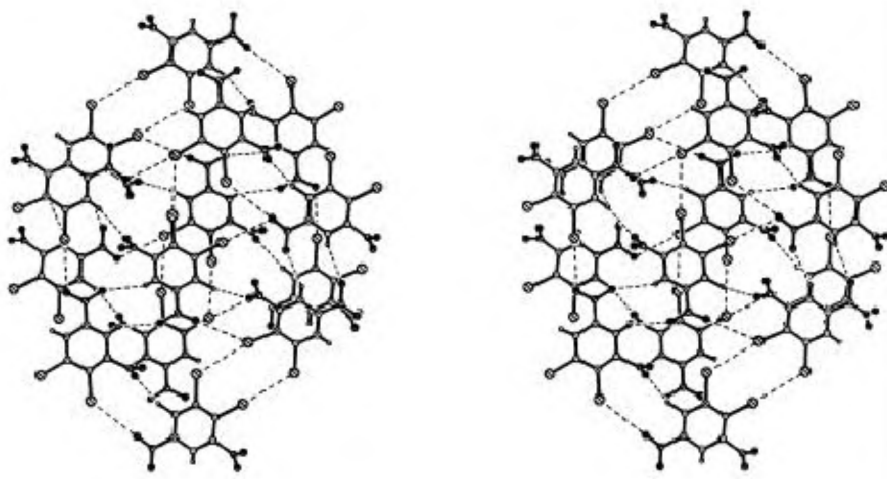


Figure 5. Stereoview of 6 showing the layer arrangement.

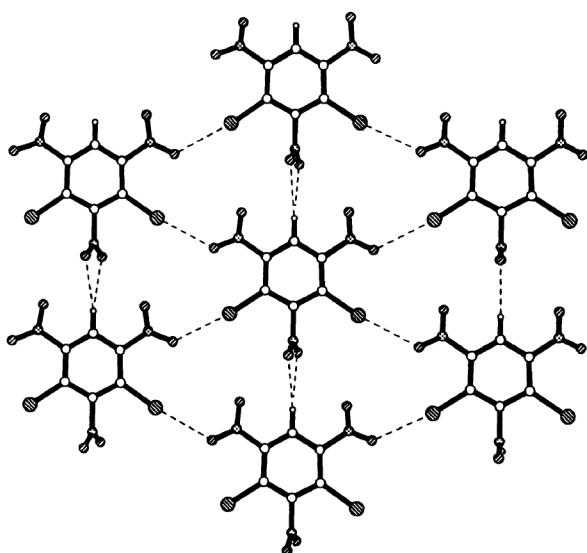


Figure 6. The hexagonal network structure in 7.

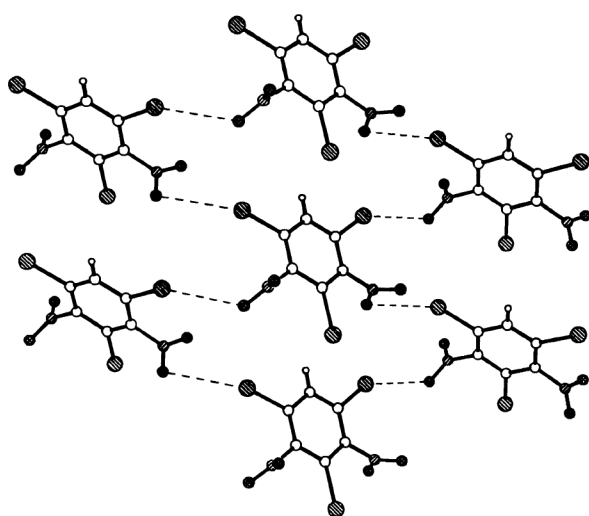


Figure 7. Crystal structure of 8.

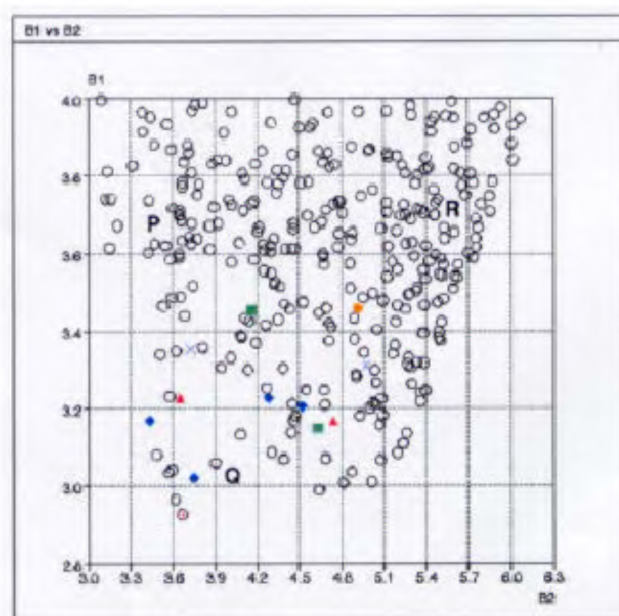


Figure 8. Scatterplot of Br...NO<sub>2</sub> interactions (P, Q and R) from the CSD. Compounds 3, 4, 5, 6, 7 and 8 are indicated as ♦, •, ■, ▲, ⊕ and ×.

group (forms the shortest Br...NO<sub>2</sub> interaction) and the out-of-plane nitro group (forms a bifurcated C–H...O hydrogen bond) are all very important to align the chromophores along the polar axis. However, most of this discussion is *post facto* rationalization. It would have been difficult to predict the crystal structures of 7 and 8, and the differences therein, in advance.

### Cambridge structural database

The three types of Br...NO<sub>2</sub> contacts denoted by P, Q and R are shown in the scatterplot given in Figure 8 representing hits from the Cambridge Structural Database<sup>18</sup>

(Version 5.24 November 2002) for error-free organic compounds with  $R < 0.10$ . Disordered structures and those with missing coordinates were excluded from the search. Of the 152 entries in the subset, 342 fragments were considered with  $\text{Br}\cdots\text{NO}_2$  interactions in the distance range of  $D_1 = 2.8$  to  $4.0 \text{ \AA}$  and  $D_2 = 2.8$  to  $6.4 \text{ \AA}$ . Figure 8 shows that the region corresponding to the **P** (symmetrical) and **R** (single point) contacts are populated. Curiously, however, most of the compounds in the present study occur in the **Q** region (unsymmetrical contacts). This may be due to steric reasons because the compounds in this study are heavily polysubstituted. The shortest  $\text{Br}\cdots\text{NO}_2$  contact found in compound **7** is noteworthy.

## Conclusions

Organic crystal structures of polyfunctional molecules may be conveniently described as networks when there is evidence of structural repetition in the form of robust supramolecular synthons. The  $\text{Br}\cdots\text{NO}_2$  synthon is one such sub-structural motif and acts as a node connection in the formation of square and hexagonal networks in a series of polybromonitrobenzenes. Structural variability in this group of compounds seems to be determined by the C–H activation and the number of out-of-plane nitro groups in the molecule.

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