

## Cocrystallized 1,2-dibromo-4,5-dimethyl-3-nitrobenzene and 1,2-dibromo-4,5,6-trimethyl-3-nitrobenzene

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## Key indicators

Single-crystal X-ray study  
 $T = 120\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$   
Disorder in main residue  
 $R$  factor = 0.030  
 $wR$  factor = 0.073  
Data-to-parameter ratio = 14.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the crystal structure of the title compound,  $\text{C}_8\text{H}_7\text{Br}_2\text{NO}_2 \cdot \text{C}_9\text{H}_9\text{Br}_2\text{NO}_2$ , the 1,2-dibromo-4,5-dimethyl-3-nitrobenzene and 1,2-dibromo-4,5,6-trimethyl-3-nitrobenzene molecules occupy the same crystallographic position, such that the aromatic H atom of the former compound is superimposed on the methyl group of the latter. The structure is thus best modelled by a 50:50 disorder of the two compounds. All non-H atoms are located on a mirror plane except the O atoms of the nitro group.

## Comment

1,2-Dibromo-4,5-dimethyl-3-nitrobenzene was required as a reagent for the synthesis of 1,2-bis(mercapto)-4,5-dimethyl-3-nitrobenzene, which can be used as a 1,2-dithiolate ligand. However, melting point measurements revealed that this compound melts over a wide temperature range and NMR spectra were more complex than expected. Therefore, a single-crystal structure determination was performed, which shows that the sample is a cocrystallized mixture of the expected material and 1,2-dibromo-4,5,6-trimethyl-3-nitrobenzene.

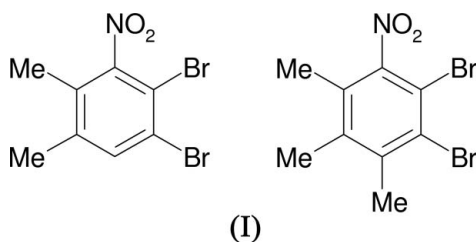
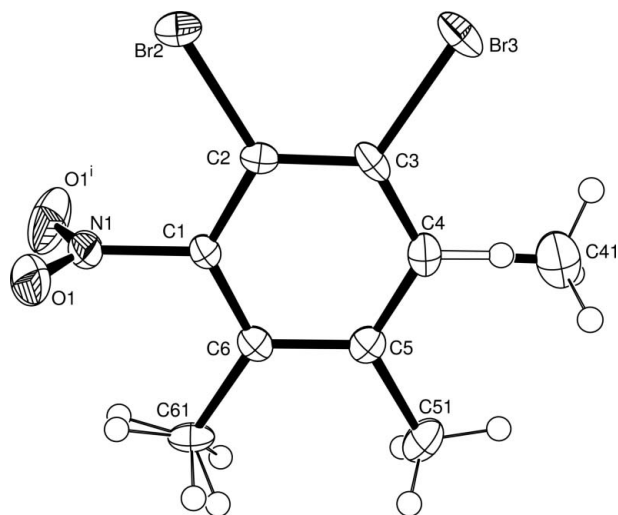


Fig. 1 shows the superimposed molecules within the crystal structure, the only difference lying in the replacement of the H atom at C4 by a methyl group. All non-H atoms are located on a crystallographic mirror plane, except the O atoms of the nitro group, which occupy general positions. The H atoms of one of the three crystallographically independent methyl groups are disordered over two orientations.

In the crystal structure, the molecules are stacked in the direction of the crystallographic  $b$  axis, but shifted in such a way that one C atom of the six-membered ring is located above and below the centroids of the six-membered rings of the neighbouring molecules (Fig. 2).

## Experimental

A donated sample of 1,2-dibromo-4,5-dimethyl-3-nitrobenzene was recrystallized from ethanol (m.p. 381–390 K). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , p.p.m.): 1,2-dibromo-4,5-dimethyl-3-nitrobenzene: 2.26 (s, 3H), 2.29 (s, 3H) (both Me), 7.54 (s, 1H, aryl-H); 1,2-dibromo-4,5,6-


**Figure 1**

The molecular structure of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as circles of arbitrary radii. [Symmetry code: (i)  $x, \frac{1}{2} - y, z$ .] Disorder of the C6 methyl group is indicated.

trimethyl-3-nitrobenzene: 2.25 (s, 3H), 2.29 (s, 3H), 2.53 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.7, 16.7, 19.8, 22.7, 112.5, 114.1, 122.9, 128.7, 131.5, 135.1, 139.5, 151.1 and 153.8. IR ( $\text{cm}^{-1}$ , KBr): 3094, 3026–2701, 1765, 1537, 1544, 1370, 1340, 1265, 1065, 895, 841, 738, 651, 532, 466.

#### Crystal data

$\text{C}_8\text{H}_7\text{Br}_2\text{NO}_2 \cdot \text{C}_9\text{H}_9\text{Br}_2\text{NO}_2$   
 $M_r = 631.96$   
 Orthorhombic,  $Pnma$   
 $a = 8.9730$  (3) Å  
 $b = 7.1165$  (2) Å  
 $c = 15.2972$  (5) Å  
 $V = 976.82$  (5) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 2.149$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 1315 reflections  
 $\theta = 2.9$ – $27.5^\circ$   
 $\mu = 8.27$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
 Rod, colourless  
 $0.60 \times 0.15 \times 0.15$  mm

#### Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)  
 $T_{\min} = 0.101$ ,  $T_{\max} = 0.289$   
 10287 measured reflections  
 1199 independent reflections

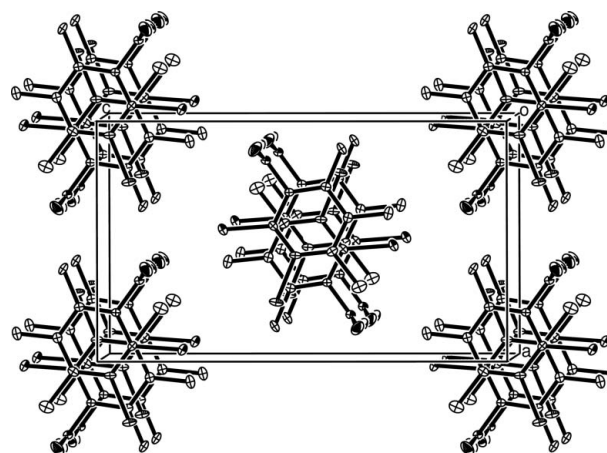
1047 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.039$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -11 \rightarrow 11$   
 $k = -9 \rightarrow 8$   
 $l = -17 \rightarrow 19$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.030$   
 $wR(F^2) = 0.073$   
 $S = 1.11$   
 1199 reflections  
 84 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2 + 1.2866P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.72$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.82$  e Å<sup>-3</sup>

The space groups  $Pnma$  and  $Pna2_1$  were permitted by the systematic absences;  $Pnma$  was selected and confirmed by the structure analysis. To check that the disorder was not an artefact of the selected space group, the structure was also solved in  $Pna2_1$  and in the triclinic spacegroup  $\bar{P}1$ . In both space groups the disorder was also evident. In addition, no superstructure reflections were found.


**Figure 2**

Part of the crystal structure of the title compound, showing the packing of molecules along [010]. Displacement ellipsoids are shown at the 30% level and H atoms have been omitted for clarity. Only one component is shown for each disordered group.

All H atoms were located in difference maps and then treated as riding atoms, with C–H distances of 0.95 Å (aromatic) or 0.98 Å (methyl), and  $U_{\text{iso}}(\text{H})$  values of  $1.2U_{\text{eq}}(\text{C})$  for aromatic and  $1.5U_{\text{eq}}(\text{C})$  for methyl H atoms. The occupancy of the disordered methyl (C41) group was initially refined freely, and converged to a low value (0.27) but with non-positive displacement parameters for this atom, so the occupancy was gradually increased to give displacement parameters similar to those of the other methyl groups. Finally, they were fixed at  $\frac{1}{2}$ , representing a 50:50 mixture of the cocrystallized molecules. The H atoms of one of the three methyl groups are disordered over two orientations with equal occupancies.

Data collection: COLLECT (Hooft, 1998); cell refinement: DENZO (Otwinowski & Minor, 1997) and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: OSCAIL (McArdle, 2003) and SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: OSCAIL and SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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