

Mohd Mustaqim Rosli,<sup>a</sup>  
Hoong-Kun Fun,<sup>a\*</sup> Beck Sim  
Lee,<sup>a</sup> Pumsak Ruanwas<sup>b</sup> and  
Suchada Chantrapromma<sup>b\*</sup>

<sup>a</sup>X-ray Crystallography Unit, School of Physics,  
Universiti Sains Malaysia, 11800 USM, Penang,  
Malaysia, and <sup>b</sup>Department of Chemistry,  
Faculty of Science, Prince of Songkla University,  
Hat-Yai, Songkhla 90112, Thailand

Correspondence e-mail: hkfun@usm.my,  
suchada.c@psu.ac.th

#### Key indicators

Single-crystal X-ray study  
 $T = 297$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.001$  Å  
Disorder in solvent or counterion  
 $R$  factor = 0.055  
 $wR$  factor = 0.175  
Data-to-parameter ratio = 31.5

For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

## Hexamethylenetetraminium 2,4-dinitrobenzoate monohydrate

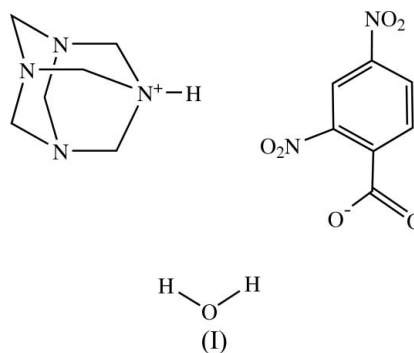
In the crystal structure of the proton-transfer compound,  $\text{C}_6\text{H}_{13}\text{N}_4^+ \cdot \text{C}_7\text{H}_3\text{N}_2\text{O}_6^- \cdot \text{H}_2\text{O}$ , the hexamethylenetetraminium and 2,4-dinitrobenzoate ions are linked by bifurcated  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds. The crystal structure is stabilized by  $\text{O}-\text{H} \cdots \text{N}$  hydrogen bonds and weak  $\text{C}-\text{H} \cdots \text{O}$  interactions to form a three-dimensional network. The benzene rings of the 2,4-dinitrobenzoate ion make a  $\pi-\pi$  interaction with a centroid-centroid distance of 3.689 (1) Å.

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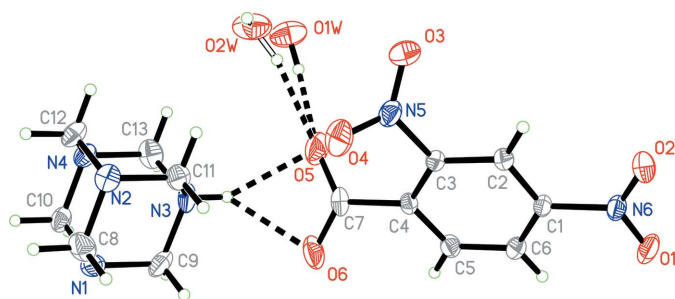
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#### Comment

The interactions of organic acids with amine bases in the solid phase have been of interest owing to their hydrogen-bonding interactions (Coupar *et al.*, 1997; Sobczyk *et al.*, 2000; Smith, Wermuth & White, 2001; Smith, Wermuth, Bott *et al.*, 2001; Fun *et al.*, 2003; Chantrapromma & Fun, 2004) and their important role in biological systems (Blow, 1976). Following our continuing studies of hydrogen-bonding interactions and phase transitions due to hydrogen bonding (Usman *et al.*, 2001; Fun *et al.*, 2003; How *et al.*, 2005; Chantrapromma *et al.*, 2006), we present here another proton-transfer compound of hexamethylenetetramine with a nitro-substituted aromatic carboxylic acid, (I).

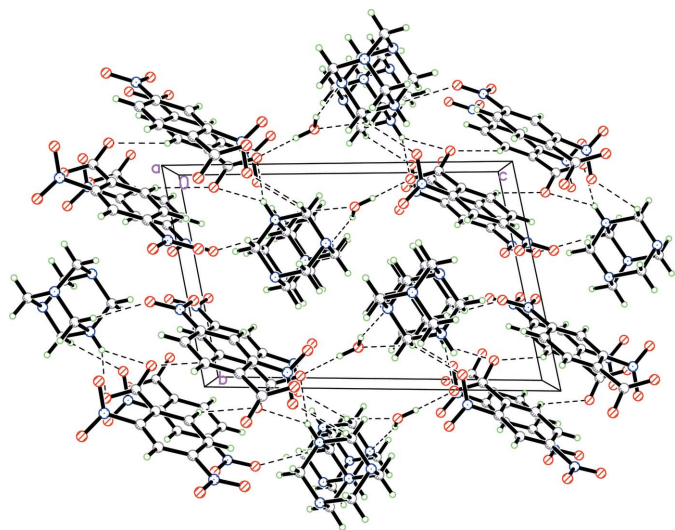


In the asymmetric unit of (I), all bond lengths and angles show normal values (Allen *et al.*, 1987). The carboxylate and the neighbouring nitro group are twisted away from the plane of the benzene ring, with torsion angles  $\text{O}5-\text{C}7-\text{C}4-\text{C}3 = 40.66$  (16) $^\circ$ ,  $\text{O}6-\text{C}7-\text{C}4-\text{C}5 = 43.87$  (15) $^\circ$ ,  $\text{O}3-\text{N}5-\text{C}3-\text{C}2 = 53.26$  (15) $^\circ$  and  $\text{O}4-\text{N}5-\text{C}3-\text{C}4 = 51.83$  (15) $^\circ$ , while the other nitro group is located almost in the plane of the benzene ring, with torsion angles  $\text{O}1-\text{N}6-\text{C}1-\text{C}6 = 0.03$  (14) $^\circ$  and  $\text{O}1-\text{N}6-\text{C}1-\text{C}2 = 179.99$  (9) $^\circ$ . The dihedral angle between the planes of the adjacent carboxylate and nitro groups is 51.3 (1) $^\circ$ . All the six-membered N/C/N/C/N/C rings of the hexamethylenetetraminium ion adopt a chair conformation, the puckering parameters  $Q$ ,  $\theta$  and  $\varphi$  being



**Figure 1**

The asymmetric unit of (I), showing 30% probability displacement ellipsoids and the atomic numbering. Hydrogen bonds are shown as dashed lines. Both disorder components are shown.

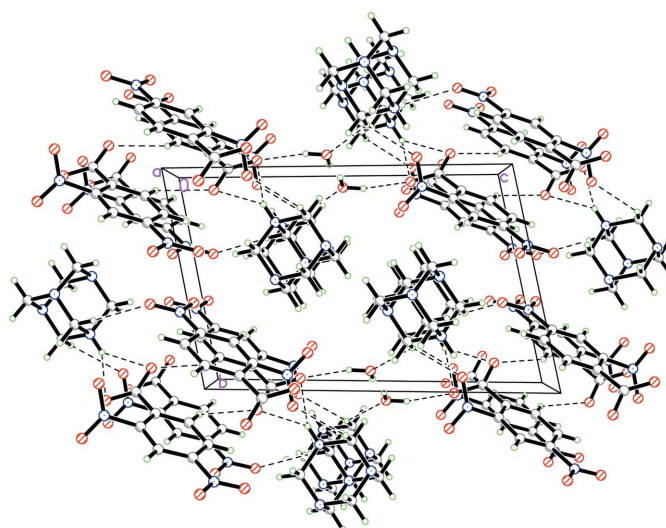


**Figure 2**

The crystal packing of (I), viewed down the *a* axis. Hydrogen bonds are shown as dashed lines. Only one disorder component (O1W) is shown.

0.598 (1) Å, 179.2 (1)° and 25 (10)°, respectively, for N1/C8/N2/C11/N3/C9, 0.579 (1) Å, 0.8 (1)° and 262 (7)°, respectively, for N1/C8/N2/C12/N4/C10, 0.590 (1) Å, 178.7 (1)° and 259 (5)°, respectively, for N1/C9/N3/C13/N4/C10, and 0.597 (1) Å, 1.4 (1)° and 153 (5)°, respectively, for N2/C11/N3/C13/N4/C12.

The hexamethylenetetraminium and 2,4-dinitrobenzoate ions are connected by bifurcated hydrogen bonds, N3—H13···O5 and N3—H13···O6 (Table 1). The 2,4-dinitrobenzoate ion also forms a hydrogen bond O1W—H1W1···O5 (O2W—H1W2···O5) with the disordered water molecule. The crystal structure of (I) is stabilized by intermolecular hydrogen bonds O1W—H1W1···N4<sup>i</sup>, C11—H9···O1<sup>iii</sup>, C13—H12···O4<sup>iii</sup>, C13—H12···O1W<sup>i</sup> and C5—H16···O6<sup>iv</sup> (symmetry codes as in Table 1), which form chains in the three-dimensional molecular network. A short contact interaction of O1···N1(1 - *x*, -1 - *y*, -*z*) [2.926 (2) Å] and a  $\pi$ - $\pi$  interaction between the benzene rings of 2,4-dinitrobenzoate ions with a centroid-centroid distance of 3.689 (1) Å also contribute to the stabilization of the crystal structure.



**Figure 3**

The crystal packing of (I), viewed down the *a* axis. Hydrogen bonds are shown as dashed lines. Only the second disorder component (O2W) is shown.

## Experimental

Compound (I) was prepared by mixing thoroughly hexamethylenetetramine (0.70 g, 5 mmol) and 2,4-dinitrobenzoic acid (1.06 g, 5 mmol), which were dissolved in acetone (100 ml), adding a few drops of water. The resulting mixture was warmed to the temperature range 313–318 K, whereupon a clear solution was obtained. The solution was then filtered and left to evaporate slowly at room temperature. Colourless single crystals suitable for X-ray diffraction studies were obtained from the solution after a few days (m.p. 447–449 K).

### Crystal data

C<sub>6</sub>H<sub>13</sub>N<sub>4</sub><sup>+</sup>·C<sub>7</sub>H<sub>3</sub>N<sub>2</sub>O<sub>6</sub><sup>-</sup>·H<sub>2</sub>O  
*M<sub>r</sub>* = 370.33  
 Triclinic, *P* $\bar{1}$   
*a* = 6.4118 (1) Å  
*b* = 9.1042 (2) Å  
*c* = 14.1521 (2) Å  
 $\alpha$  = 77.986 (1)°  
 $\beta$  = 80.464 (1)°  
 $\gamma$  = 85.585 (1)°

*V* = 796.09 (2) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.545 Mg m<sup>-3</sup>  
 Mo *K* $\alpha$  radiation  
 $\mu$  = 0.13 mm<sup>-1</sup>  
*T* = 297 (2) K  
 Block, colourless  
 0.55 × 0.43 × 0.33 mm

### Data collection

Bruker SMART APEX2 CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2005)  
*T<sub>min</sub>* = 0.855, *T<sub>max</sub>* = 0.959

23506 measured reflections  
 7817 independent reflections  
 5034 reflections with *I* > 2 $\sigma$ (*I*)  
*R<sub>int</sub>* = 0.023  
 $\theta_{\max}$  = 37.2°

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.055  
*wR* (*F*<sup>2</sup>) = 0.175  
*S* = 1.06  
 7817 reflections  
 248 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0818P)^2 + 0.0892P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{Å}^{-3}$

**Table 1**  
Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1W—H1W1···O5	0.84 (1)	1.80 (1)	2.633 (2)	176 (1)
O2W—H1W2···O5	0.87 (1)	2.06 (1)	2.912 (3)	167 (1)
N3—H13···O5	0.88	2.18	2.935 (2)	144
N3—H13···O6	0.88	2.20	2.916 (2)	138
O1W—H2W1···N4 <sup>i</sup>	0.83 (1)	2.26 (1)	3.053 (3)	158 (1)
C11—H9···O1 <sup>ii</sup>	0.97	2.42	3.352 (2)	159
C13—H12···O4 <sup>iii</sup>	0.97	2.51	3.207 (2)	128
C13—H12···O1W <sup>†</sup>	0.97	2.59	3.069 (3)	110
C5—H16···O6 <sup>iv</sup>	0.93	2.53	3.264 (2)	136

Symmetry codes: (i)  $-x + 2, -y, -z + 1$ ; (ii)  $-x + 1, -y, -z$ ; (iii)  $x + 1, y, z$ ; (iv)  $-x + 2, -y, -z$ .

All C-bound H atoms were placed in calculated positions with C—H distances in the range 0.93–0.97 Å and refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The O-bound and N-bound H atoms were located in a difference map. For the O-bound H atoms the positions were freely refined with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ , while for the N-bound H atom the positional and isotropic displacement parameters were constrained as riding, with N—H = 0.88 Å and  $U_{\text{iso}}(\text{H}) = 0.063$ . The water molecule is disordered over two sites with relative occupancies of 0.574 (5) and 0.426 (5).

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

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