Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

The 143 and 300 K polymorphs of hexamethylenetetraminium 2,4-dinitrophenolate monohydrate

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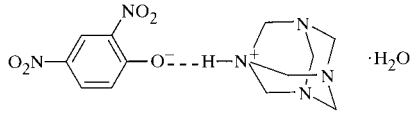
Received 7 August 2001
Accepted 9 October 2001

The title compound, 3,5,7-triaza-1-azoniatricyclo[3.3.1.1^{3,7}]-decane 2,4-dinitrophenolate monohydrate, $C_6H_{13}N_4^+\cdot C_6H_3N_2O_5^-\cdot H_2O$, the 1:1 hydrate adduct of hexamethylenetetramine (HMT) and 2,4-dinitrophenol, undergoes a temperature phase transition. In the room-temperature phase, the adduct crystallizes in the monoclinic $P2_1/m$ space group, whereas in the low-temperature phase, the adduct crystallizes in the triclinic $P\overline{1}$ space group. This phase transition is reversible, with the transition temperature at 273 K, and the phase transition is governed by hydrogen bonds and weak interactions. In both these temperature-dependent polymorphs, the crystal structure is alternately layered with sheets of hexamethylenetetramine and sheets of dinitrophenol stacked along the *c* axis. The hexamethylenetetramine and dinitrophenol moieties are linked by intermolecular hydrogen bonds. The water molecule in the adduct plays an important role, forming O—H···O hydrogen bonds which, together with C—H···O hydrogen bonds, bridge the adducts into molecular ribbons. Extra hydrogen bonds and weak interactions exist for the low-temperature polymorph and these interconnect the molecular ribbons into a three-dimensional packing structure. Also in these two temperature-dependent polymorphs, dinitrophenol acts as a hydrogen-bond acceptor and HMT acts as a hydrogen-bond donor.

Comment

The N—H···O-type of hydrogen bond is a versatile synthon in crystal engineering (Fan *et al.*, 1994; Desiraju, 1995). Phenols, in general, are strong acids and tend to form N—H···O hydrogen bonds with aromatic or tertiary amines. Therefore, a number of studies have been conducted into phenol–hexamethylenetetramine adducts (with various ratios) to design and construct a variety of hydrogen-bonding systems. In general, in the adducts of hexamethylenetetramine (HMT) with simple phenols, HMT acts as a mono-, bis- or tris-acceptor of hydrogen bonds (Jordan & Mak, 1970; Mak *et al.*, 1977, 1978; Mahmoud & Wallwork, 1979; Coupar, Glidewell & Ferguson, 1997; Coupar, Ferguson *et al.*, 1997).

We have now isolated the crystalline form of the hydrate, (I), of the 1:1 stoichiometric adduct of 2,4-dinitrophenol with HMT. The adduct undergoes a phase transition when the temperature is lowered. The room-temperature monoclinic $P2_1/m$ phase transforms into a low-temperature triclinic $P\overline{1}$ phase upon lowering the temperature below 273 K. The phase transition is reversible. We report here the crystal structures of these two temperature-dependent polymorphs, namely the monoclinic polymorph at 300 K and the triclinic polymorph at 143 K (Fig. 1).



(I)

In these two temperature-dependent polymorphs, HMT, in an unusual manner, acts as a hydrogen-bond donor in the N—H···O hydrogen bonds observed in these structures.

At 300 K, the asymmetric unit contains one half of a HMT molecule and the monoclinic unit cell contains two adducts. One half of the HMT molecule is related to the other by a centre of symmetry. At 143 K, the asymmetric unit contains the complete adduct and the triclinic unit cell also contains two adducts. In both these space groups, the geometry of the dinitrophenol and HMT moieties are as expected. The dinitrophenol molecule transfers an H atom from the hydroxy group to the HMT molecule and becomes negatively charged, with the transfered H atom being localized at the N3 atom of HMT, making it postively charged. A similar effect was also observed in the adduct of HMT with azelaic acid (Hostettler *et al.*, 1999).

In the present adduct, the transfer of the H atom from the hydroxy group was followed by an increase in the delocalization of the π-electron, resulting in slight distortions in the N—O, N—C and O—C bond distances of the functional groups of the dinitrophenol moiety, whereas due to the localization of the positive charge at the N3 atom, the C—N3 bond distance is as expected for a C—N single bond in a trimethylammonium ion (Allen *et al.*, 1987). All other bond lengths and angles in (I) have normal values and are listed in Table 1 for the monoclinic and Table 3 for the triclinic polymorph.

In both polymorphs, the dinitrophenol moiety is essentially planar, with atom O3 deviating by a maximum of 0.0 Å at 300 K and 0.080 (3) Å at 143 K. All the six-membered C—N—C—N—C—N rings of HMT adopt a chair conformation with almost the same puckering parameters (Cremer & Pople, 1975); a table of these puckering parameters is available in the supplementary material. These facts rule out the possibility that the temperature phase transformation is due to conformational changes since there are not many differences

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between the structures of the two temperature-dependent polymorphs. However, there are differences in the hydrogen-bond motifs of these two polymorphs.

In both polymorphs, there are conventional hydrogen bonds (Table 2 and Table 4) and C9—H9*B*···O4 and N3—H13N···O4 weak interactions [C9···O4^{i} and C9—H9*B*···O4^{i} = 3.136 (2) Å and 117 (1)° at 300 K, and 3.114 (3) Å and 117 (2)° at 143 K; N3···O4^{ii} and N3—H13N···O4^{ii} = 2.873 (2) Å and 122 (3)° at 300 K, and 2.843 (3) Å and 125 (3)° at 143 K; symmetry codes: (i) $1-x$, $\frac{1}{2}+y$, $1-z$; (ii) $1-x$, $\frac{1}{2}+y$, $1-z$]. Figs. 2 and 3 show the packing diagrams, and indicate the hydrogen bonds and weak interactions. The crystal structure of the adduct in both polymorphs is built from molecular sheets of HMT molecules and molecular sheets of dinitrophenol molecules alternately stacked along the *c* axis. HMT unusually adopts the role of a donor in these intermolecular N—H···O hydrogen bonds, *i.e.* atom N3 acts as donor to the dinitrophenol O4 and O5 atoms. The N···O distances in the N—H···O hydrogen bonds in the two polymorphs of adduct (I) are comparable with those observed for the O—H···N hydrogen bonds in other HMT–phenol adducts (Mak *et al.*, 1978; Mahmoud & Wallwork, 1979; Coupar, Glidewell & Ferguson, 1997; Coupar, Ferguson *et al.*, 1997).

The water molecule in the adduct plays an important role in forming O—H···O hydrogen bonds, which together with an intermolecular C—H···O hydrogen bond, *i.e.* C5—H5*A*···O3, bridge the dinitrophenol molecules and link the adducts into molecular ribbons parallel to the *b* axis. These molecular ribbons pack on top of one another.

At low temperatures, two extra weak intramolecular interactions [C9*A*···O4 3.086 (3) Å and C9*A*—H9*AB*···O4

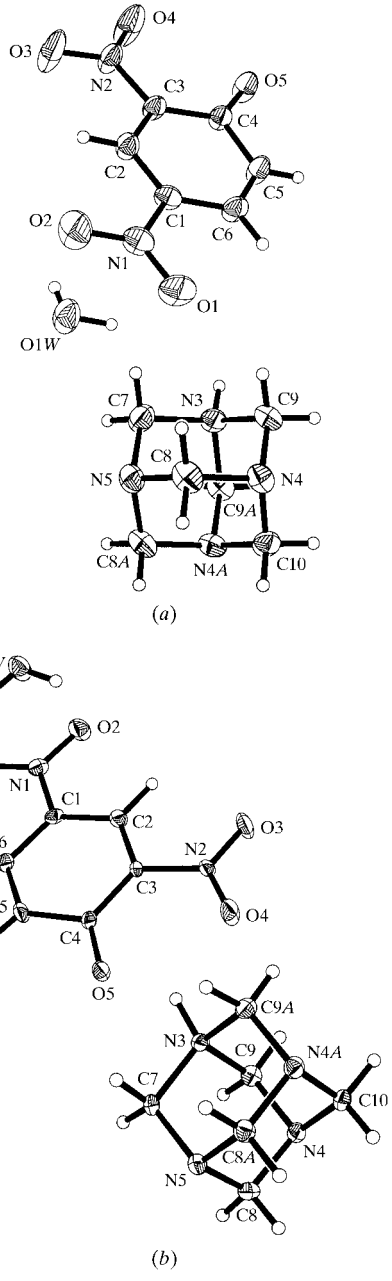

Figure 1
The structure of the title adduct showing 50% probability displacement ellipsoids and the atom-numbering scheme for (*a*) the monoclinic (300 K) polymorph and (*b*) the triclinic (143 K) polymorph of adduct (I).

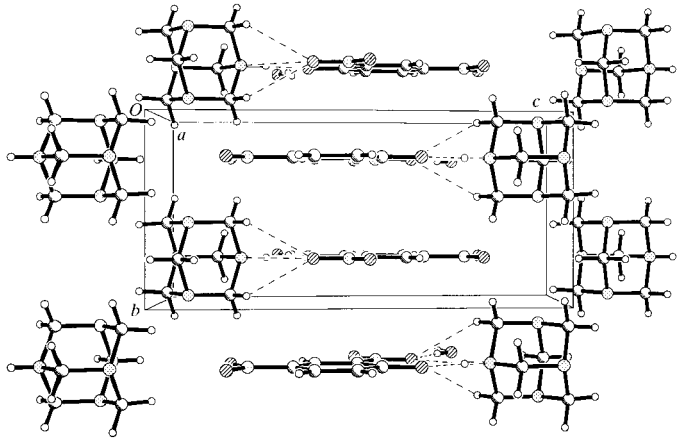

Figure 2
Packing diagram of the monoclinic polymorph of adduct (I).

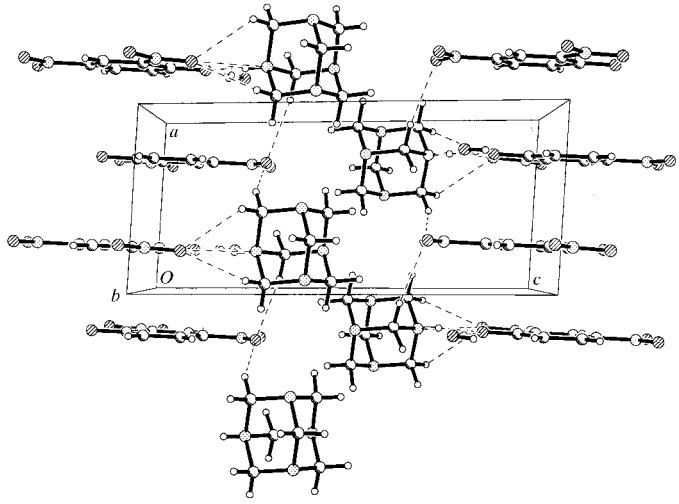

Figure 3
Packing diagram of the triclinic polymorph of adduct (I).

123 (2)°, and C6···O1 2.734 (3) Å and C6—H6*A*···O1 101 (2)°] and two extra intermolecular C—H···O hydrogen bonds (Table 4) were observed; the extra weak interactions and hydrogen bonds link the four C atoms of the HMT moiety and the two O atoms of the dinitrophenol moiety, *i.e.* they link atoms C9 and C9*A* with atoms O1 and O4, respectively, and they link atoms C7 and C9 with atom O1. These extra intermolecular C—H···O hydrogen bonds connect the molecular ribbons into a three-dimensional arrangement and stabilize the triclinic polymorphic structure.

Since the only difference between the two polymorphs is in the packing, which is governed by the different hydrogen-bonding and weak interaction patterns, we can attribute this reversible temperature phase transition to the presence or absence of these extra hydrogen-bonding and weak interactions.

In conclusion, the transition observed in the 1:1 HMT–2,4-dinitrophenol hydrate adduct is a new type of reversible temperature phase transistion governed by hydrogen-bonding and weak interactions. We have also observed similar transition phenomena in other complexes which are presently under investigation.

Experimental

HMT (1.4 g, 10 mmol) and 2,4-dinitrophenol (1.8 g, 10 mmol) were mixed and dissolved in acetone (30 ml) together with a few drops of water. The resulting mixture was heated until a clear solution was obtained. The solution was then filtered and the filtrate was left to evaporate slowly in air. Yellow single crystals suitable for X-ray diffraction studies were obtained after a few days.

Monoclinic (300 K) polymorph of adduct (I)

Crystal data

$C_6H_{13}N_4^+\cdot C_6H_3N_2O_5^-\cdot H_2O$
M_r = 342.32
Monoclinic, $P2_1/m$
a = 7.8610 (5) Å
b = 6.5980 (4) Å
c = 14.4339 (9) Å
β = 94.915 (1)°
V = 745.89 (8) Å^3
Z = 2
D_x = 1.524 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3560 reflections
θ = 1.4–29.6°
μ = 0.12 mm^{-1}
T = 300 (2) K
Block, yellow
0.42 × 0.24 × 0.20 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.950, T_{max} = 0.976
5088 measured reflections
1900 independent reflections
1288 reflections with $I > 2\sigma(I)$
R_{int} = 0.069
θ_{max} = 28.0°
$h = -10 \rightarrow 9$
$k = -8 \rightarrow 7$
$l = -19 \rightarrow 18$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.144
S = 0.95
1900 reflections
178 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0622P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.145 (17)

Table 1
Selected geometric parameters (Å, °) for the monoclinic (300 K) polymorph of adduct (I).

N1—O2	1.234 (3)	N3—C7	1.519 (3)
N1—O1	1.243 (3)	N4—C9	1.438 (2)
N1—C1	1.441 (3)	N4—C10	1.4666 (19)
N2—O4	1.213 (3)	N4—C8	1.468 (2)
N2—O3	1.219 (3)	N5—C7	1.446 (3)
N2—C3	1.440 (3)	N5—C8	1.473 (2)
N3—C9	1.510 (2)	O5—C4	1.264 (3)
O2—N1—O1	122.4 (2)	C10—N4—C8	108.35 (15)
O4—N2—O3	120.4 (2)	C7—N5—C8	109.10 (12)
C9^i—N3—C9	108.61 (18)	C8^i—N5—C8	107.76 (19)
C9^i—N3—C7	108.71 (11)	N5—C7—N3	109.74 (18)
C9—N3—C7	108.71 (11)	N4—C8—N5	111.82 (13)
C9—N4—C10	108.88 (14)	N4—C9—N3	109.65 (13)
C9—N4—C8	109.75 (14)	N4—C10—N4^i	111.77 (18)

Symmetry code: (i) $x, \frac{3}{2} - y, z$.

Table 2
Hydrogen-bonding geometry (Å, °) for the monoclinic (300 K) polymorph of adduct (I).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H13N···O5^i	0.85 (3)	1.85 (3)	2.657 (2)	159 (3)
O1W—H11W···O5^i	0.96 (3)	1.86 (3)	2.816 (3)	177 (3)
O1W—H21W···O4^{ii}	0.73 (5)	2.35 (5)	3.037 (3)	159 (5)
C5—H5A···O3^{iii}	0.88 (3)	2.48 (3)	3.164 (3)	135 (2)

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, 1 - z$; (ii) $-x, \frac{1}{2} + y, 1 - z$; (iii) $1 + x, y, z$.

Triclinic (143 K) polymorph of adduct (I)

Crystal data

$C_6H_{13}N_4^+\cdot C_6H_3N_2O_5^-\cdot H_2O$
M_r = 342.32
Triclinic, $P\overline{1}$
a = 6.3877 (4) Å
b = 7.9017 (5) Å
c = 14.4042 (9) Å
α = 84.412 (1)°
β = 86.367 (1)°
γ = 89.304 (1)°
V = 722.11 (8) Å^3
Z = 2
D_x = 1.574 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3560 reflections
θ = 1.4–29.6°
μ = 0.13 mm^{-1}
T = 143 (2) K
Block, yellow
0.42 × 0.24 × 0.20 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.948, T_{max} = 0.975
4841 measured reflections
3227 independent reflections
2201 reflections with $I > 2\sigma(I)$
R_{int} = 0.073
θ_{max} = 28.0°
$h = -8 \rightarrow 6$
$k = -10 \rightarrow 10$
$l = -18 \rightarrow 18$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.087
$wR(F^2)$ = 0.206
S = 0.96
3227 reflections
281 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.077P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.099 (15)

Table 3
Selected geometric parameters (Å, °) for the triclinic (143 K) polymorph of adduct (I).

N1—O2	1.230 (3)	N4—C8	1.469 (3)
N1—O1	1.250 (3)	N4—C10	1.480 (3)
N1—C1	1.446 (3)	N4*A*—C9*A*	1.446 (3)
N2—O3	1.232 (3)	N4*A*—C8*A*	1.468 (3)
N2—O4	1.241 (3)	N4*A*—C10	1.473 (3)
N2—C3	1.440 (3)	N5—C7	1.452 (3)
N3—C9*A*	1.514 (3)	N5—C8	1.473 (3)
N3—C9	1.516 (3)	N5—C8*A*	1.476 (3)
N3—C7	1.526 (3)	O5—C4	1.269 (3)
N4—C9	1.447 (3)		
O2—N1—O1	122.3 (2)	C8*A*—N4*A*—C10	108.5 (2)
O3—N2—O4	121.1 (2)	C7—N5—C8	108.7 (2)
C9*A*—N3—C9	108.9 (2)	C7—N5—C8*A*	108.8 (2)
C9*A*—N3—C7	108.2 (2)	C8—N5—C8*A*	108.3 (2)
C9—N3—C7	108.6 (2)	N5—C7—N3	109.75 (19)
C9—N4—C8	109.0 (2)	N4—C8—N5	112.3 (2)
C9—N4—C10	108.4 (2)	N4*A*—C8*A*—N5	112.07 (19)
C8—N4—C10	108.8 (2)	N4—C9—N3	110.08 (19)
C9*A*—N4*A*—C8*A*	109.2 (2)	N4*A*—C9*A*—N3	109.7 (2)
C9*A*—N4*A*—C10	109.48 (19)	N4*A*—C10—N4	111.5 (2)

Table 4
Hydrogen-bonding geometry (Å, °) for the triclinic (143 K) polymorph of adduct (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H13N···O5	0.79 (3)	1.91 (3)	2.644 (3)	155 (3)
O1*W*—H11*W*···O5^{i}	0.94 (4)	1.88 (4)	2.821 (3)	176 (3)
O1*W*—H21*W*···O4^{ii}	0.87 (3)	2.27 (4)	3.064 (3)	152 (3)
C5—H5*A*···O3^{iii}	0.93 (3)	2.42 (3)	3.188 (3)	140 (2)
C7—H7*B*···O1^{i}	0.99 (3)	2.49 (3)	3.462 (3)	168 (2)
C9—H9*A*···O1^{iv}	0.98 (3)	2.56 (3)	3.452 (3)	151 (2)

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

For the two polymorphs, all the H atoms were located from the difference map and were refined isotropically [C—H = 0.87 (3)–1.03 (2) Å].

For both compounds, data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL, PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 305/PFIZIK/610961. AU thanks Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1495). Services for accessing these data are described at the back of the journal.

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