

Hydrogen-bond patterns in the congruent complex 4-nitrophenol–acetamide (1/1)

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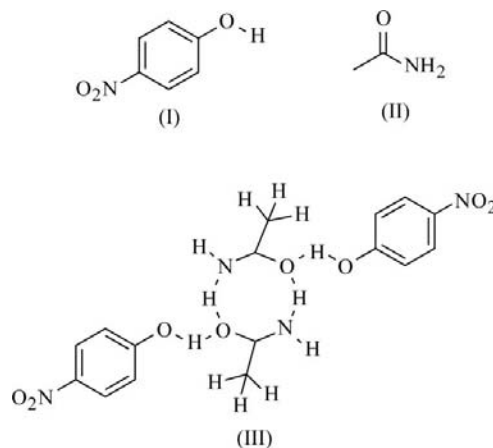
Fusion of 4-nitrophenol and acetamide in a 1:1 molar ratio gives the title product, $C_6H_5NO_3 \cdot C_2H_5NO$, (III), which has the character of a pure covalently bonded compound, having a high sharp melting point. Complex (III) (m.p. 371.9–372.9 K) can be recrystallized from various solvents and forms eutectics with either acetamide or 4-nitrophenol. Similar fusion of mixtures of acetamide and 2-nitrophenol yields no complex similar to (III) and mixtures of acetamide and 3-nitrophenol produce only a weak low-melting complex. The significance of this study lies in its demonstration, *via* graph set analysis, that some of the patterns found individually in crystalline acetamide or 4-nitrophenol have been preserved in crystals of complex (III), while several higher order graph sets are produced in (III) due to new hydrogen bonds involving the nitro group. In particular, large hydrogen-bonded rings are formed together with helical chains.

Comment

We report here the structure and graph set analysis of the congruent 1:1 molar compound 4-nitrophenol–acetamide (1/1), (III) (m.p. 371.9–372.9 K), which forms eutectics with each of its two components, *viz.* 4-nitrophenol, (I), and acetamide, (II) (Dzhelomanova *et al.*, 1956). This molar compound crystallizes with $Z' = 2$ (Fig. 1) and retains some of the hydrogen-bond patterns observed in the crystal structure of the single components (Etter *et al.*, 1990; Etter, 1990; Bernstein *et al.*, 1995).

4-Nitrophenol, (I), has a relatively high melting point (386 K) and crystallizes in two polymorphs (Coppens & Schmidt, 1965*a,b*; Kulkarni *et al.*, 1998; Wójcik & Mossakowska, 2006). The crystal structures of (I) are characterized by hydrogen bonding between hydroxyl and nitro groups of adjacent molecules, forming endless continuous chains which are described as $C(8)$, creating a herring-bone pattern (Coppens & Schmidt, 1965*a,b*; Wójcik & Mossakowska, 2006).

Acetamide, (II), is also high melting (353 K) for such a simple compound and its structure is characterized by multiple $N-H \cdots O(C)$ bonds. This small molecule crystallizes in two forms. The more common is the orthorhombic form, which contains two molecules in the asymmetric unit (Hamilton, 1965; Jeffrey *et al.*, 1980; Ottersen, 1975), and the second is a



more unusual rhombohedral form with only one molecule in the asymmetric unit (Denne & Small, 1971; Senti & Harker, 1940). These two forms establish different hydrogen-bond patterns. The motifs in the orthorhombic form are described as $C(4)C(4)DD$ and in the rhombohedral form as $C(4)C(4)$, reflecting the endless chains formed at the first level graph set in both forms (Bernstein *et al.*, 1995). At the second level graph set, both forms generate ring patterns, *viz.* $R_2^2(8)$ in the orthorhombic form and $R_6^3(12)$ in the rhombohedral form (Bernstein *et al.*, 1995). In the orthorhombic form, the ring pattern is created through two $N-H \cdots O(C)$ hydrogen bonds between the two molecules present in the asymmetric unit (Bernstein *et al.*, 1995). In the rhombohedral form, the ring is created through $N-H \cdots O(C)$ hydrogen bonds amongst four neighbouring acetamide molecules (Bernstein *et al.*, 1995).

In the complex, (III), the four independent molecules present in the asymmetric unit establish six different hydrogen bonds (Fig. 1 and Table 1). These bonds have been labelled *a–f* to help in the assignment of the patterns formed (Etter *et al.*,

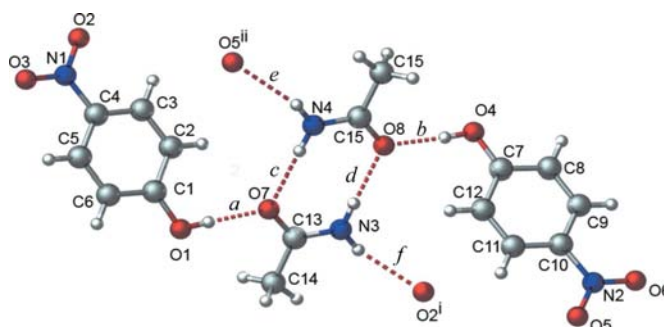


Figure 1
Acetamide molecules form dimers through $N-H \cdots O$ hydrogen bonds (*c* and *d*; dashed lines). These dimers form a three-dimensional network with 4-nitrophenol molecules through $N-H \cdots O(N)$, $C-H \cdots O(N)$ and $O-H \cdots O$ hydrogen bonds (*a*, *b*, *e* and *f*; dashed lines). [Symmetry codes: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$].

1990; Etter, 1990; Bernstein *et al.*, 1995). Surprisingly, although complex (III) forms six different hydrogen bonds, it only creates finite D patterns (Table 2). The D motifs, which are present in the orthorhombic form of acetamide, are retained in complex (III). In this case, bonds c and d generate identical D motifs to those observed in acetamide (Table 2). The other $N-H \cdots O(C)$ bond in acetamide (II) generates the $C(4)$ motif. In complex (III), this $C(4)$ motif is not retained because atoms H4B and H3B are hydrogen bonded, respectively, to $O5^i$ and $O2^i$, thereby establishing two new D motifs (e and f ; Fig. 1; see Table 1 for symmetry codes).

In 4-nitrophenol, (I), a single chain is formed through $O-H \cdots O(N)$ hydrogen bonding between the hydroxyl H atom of one molecule and a nitro O atom of a neighbouring molecule. This pattern is not retained in the crystal structure of complex (III), in which the hydroxyl H1 and H4 atoms establish new $O-H \cdots O(C)$ hydrogen bonds to amide atoms O7 and O8, thereby creating two D patterns (a and b ; Table 2 and Fig. 2). Thus, at the first level graph set, compound (III) is described as $N_1 = DDDDDD$, reflecting the large number of molecules present in the unit cell.

At the second level of the graph set, more of the patterns generated in (III) are ones retained from structures seen in the individual components (I) and (II). In the orthorhombic form of the single amide component (II), dimers are formed from two $N-H \cdots O(C)$ bonds. This feature is retained in complex (III) and dimers are formed through bonds c and d (Fig. 1 and Table 2). Thus, the $R_2^2(8)$ ring pattern observed in complex

(III) is identical to that observed in the isolated amide (II). The $C(4)$ chains formed through $N-H \cdots O(C)$ hydrogen bonds between pairs of molecules in (II) (Bernstein *et al.*, 1995) are not retained in complex (III). In the latter, the amide H atoms, which are not involved in dimer formation, instead establish hydrogen bonds with nitrophenol to create a chain of alternating (I) and (II) units. Two $C_2^2(12)$ chains are created by the pair a/f and another by the pair b/e (Fig. 2). The chains are symmetrically different and run parallel to each other along the c axis. These chains form a wave-type structure that is held together through dimers of acetamide forming a pleated sheet (Fig. 2). They are identical to the 'flat' features observed in the structures of pure components (I) and (II), but in complex (III) the chains adopt the pleated sheet form (Fig. 2). No other patterns are present at this level; therefore, the overall second level graph set for compound (III) is described as $N_2 = R_2^2(8)C_2^2(12)C_2^2(12)$, reflecting the rings and chains observed at this level.

The structures of pure components (I) and (II) do not have any higher level graph sets of hydrogen-bond patterns but their complex (III) does. This pattern is formed by combining bonds a, c, b, e, d and f or a, d, b, e, c and f (Fig. 2), which combinations describe two $C_5^5(22)$ chains. These chains include the acetamide dimers and are better described as a chain of rings. Thus, the hydrogen-bond patterns at the sixth level graph set for complex (III) are described as $N_6 = C_5^5(22)[R_2^2(8)]$. No other patterns were observed at higher level graph sets for complex (III).

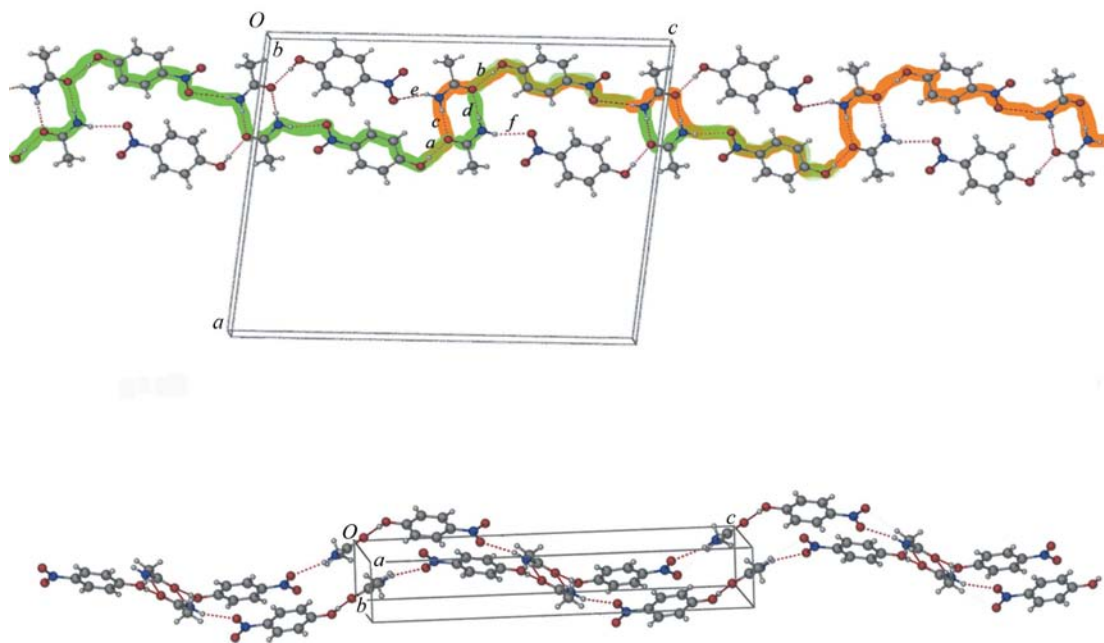


Figure 2

Intercalating chains of molecules of (I) and (II) run along the c axis in complex (III) (top). The symmetrically different chains of rings are interconnected through the formation of dimers of (II). These chains create a wave-like pattern (pleated sheet) (bottom).

Experimental

4-Nitrophenol and acetamide were used as provided (Aldrich and Acros). 4-Nitrophenol (5 g, 35.9 mmol) and acetamide (2.1 g, 35.9 mmol) were weighed into a conical flask. The flask was heated at 373 K until both reagents had melted. The yellow liquid was allowed to cool to room temperature and the resulting yellow solid was recrystallized as plates from toluene [m.p. 371.9–372.9 K; literature 369 K (Dzhelomanova *et al.*, 1956)].

Crystal data

$C_6H_5NO_3 \cdot C_2H_5NO$ $V = 1832.3 (5) \text{ \AA}^3$
 $M_r = 198.18$ $Z = 8$
 Monoclinic, $P2_1/c$ Mo $K\alpha$ radiation
 $a = 20.370 (3) \text{ \AA}$ $\mu = 0.12 \text{ mm}^{-1}$
 $b = 3.7506 (6) \text{ \AA}$ $T = 100 (2) \text{ K}$
 $c = 24.070 (3) \text{ \AA}$ $0.5 \times 0.4 \times 0.1 \text{ mm}$
 $\beta = 94.873 (3)^\circ$

Data collection

Bruker SMART APEX diffractometer 3239 independent reflections
 2683 reflections with $I > 2\sigma(I)$
 8627 measured reflections $R_{int} = 0.142$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.070$ 257 parameters
 $wR(F^2) = 0.185$ H-atom parameters constrained
 $S = 1.08$ $\Delta\rho_{max} = 0.40 \text{ e \AA}^{-3}$
 3239 reflections $\Delta\rho_{min} = -0.28 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N3-H3A \cdots O8$	0.88	2.05	2.927 (3)	172
$N3-H3B \cdots O2^i$	0.88	2.21	3.036 (3)	156
$N4-H4A \cdots O7$	0.88	2.11	2.976 (3)	170
$N4-H4B \cdots O5^{ii}$	0.88	2.29	3.129 (3)	161
$O1-H1 \cdots O7$	0.84	1.77	2.613 (3)	176
$O4-H4 \cdots O8$	0.84	1.79	2.624 (3)	176

Symmetry codes: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

All H atoms were treated as riding atoms, with $C-H = 0.95$ or 0.98 \AA , $N-H = 0.88 \text{ \AA}$ and $O-H = 0.84 \text{ \AA}$, and with $U_{iso}(H) = kU_{eq}(\text{carrier})$, where $k = 1.2$ or 1.5 .

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT (Bruker, 1998); program(s) used to solve

Table 2

Unitary motifs (on-diagonal) and binary graph sets (off-diagonal) for complex (III).

Type of hydrogen bond	a	b	c	d	e	f
a	D					
b	-	D				
c	-	-	D			
d	-	-	$R_2^2(8)$	D		
e	-	$C_2^2(12)$	-	-	D	
f	$C_2^2(12)$	-	-	-	-	D

structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Bruker, 2000); software used to prepare material for publication: SHELXTL and PLATON (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3203). Services for accessing these data are described at the back of the journal.

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