

3,4-Di-2-pyridyl-1,2,5-oxadiazole and  
its perchlorate salt

Na Liu, Ai-Ling Cheng and En-Qing Gao\*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, Shanghai 200062, People's Republic of China

Correspondence e-mail: eqgao@chem.ecnu.edu.cn

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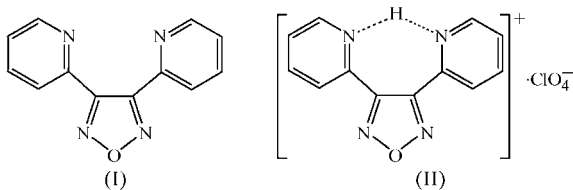
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In 3,4-di-2-pyridyl-1,2,5-oxadiazole (dpo),  $C_{12}H_8N_4O$ , each molecule resides on a twofold axis and interacts with eight neighbours *via* four  $C-H\cdots N$  and four  $C-H\cdots O$  interactions to generate a three-dimensional hydrogen-bonded architecture. In the perchlorate analogue, 2-[3-(2-pyridyl)-1,2,5-oxadiazol-4-yl]pyridinium perchlorate,  $C_{12}H_9N_4O^+ \cdot ClO_4^-$  or  $[Hdpo]ClO_4$ , the  $[Hdpo]^+$  cation is bisected by a crystallographic mirror plane, and the additional H atom in the cation is shared by the two pyridyl N atoms to form a symmetrical intramolecular  $N\cdots H\cdots N$  hydrogen bond. The cations and perchlorate anions are linked through  $C-H\cdots O$  hydrogen bonds and  $\pi-\pi$  stacking interactions to form one-dimensional tubes along the *b*-axis direction.

## Comment

Because of the well known importance of  $D-H\cdots A$  hydrogen bonds in supramolecular, biological and materials systems (Steiner, 2002), these non-covalent interactions, ranging from strong interactions involving  $O-H$  and  $N-H$  to weak interactions involving  $C-H$ , continue to be the subject of intense study, as well as a putative tool for engineering organic and organometallic solids (Desiraju & Steiner, 1999; Desiraju, 1996; Braga & Grepioni, 2000; Baures *et al.*, 2006; Maly *et al.*, 2006). In this paper, we report the structures of an oxadiazole compound, 3,4-di-2-pyridyl-1,2,5-oxadiazole (dpo), (I), and its perchlorate,  $[Hdpo]ClO_4$ , (II).

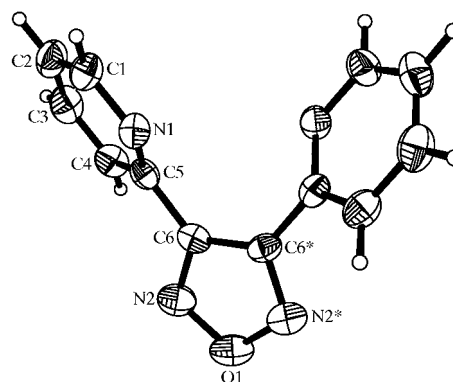


The molecular structure of dpo is shown in Fig. 1. The molecule resides on a twofold axis that passes through the O atom and the middle of the C—C bond in the oxadiazole ring. The dihedral angle between the oxadiazole ring and the

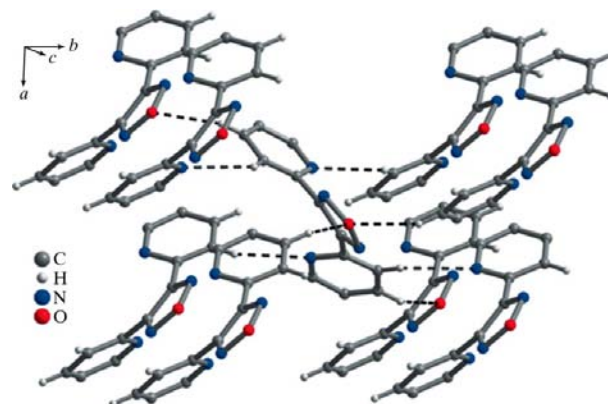
pyridyl ring is  $140.1(1)^\circ$ , and that between the two pyridyl rings is  $56.78(7)^\circ$ , indicating a significant deviation of the molecule from planarity.

In the crystal structure of (I), dpo molecules interact through weak  $C-H\cdots O$  and  $C-H\cdots N$  intermolecular interactions (Fig. 2 and Table 1). Each pyridyl group participates in  $C-H\cdots O$ ,  $C-H\cdots N$  and  $N\cdots H-C$  interactions through C3—H3A, C4—H4A and N1, respectively, to three adjacent molecules, and oxadiazole atom O1 acts as a bifurcated acceptor in two  $O\cdots H-C$  interactions with the pyridyl C3—H3A groups of two adjacent molecules. Thus, each dpo molecule is linked to eight adjacent molecules through four  $C-H\cdots O$  and four  $C-H\cdots N$  interactions, generating a three-dimensional supramolecular structure.

The molecular structure of  $[Hdpo]ClO_4$  is shown in Fig. 3. A difference Fourier map indicated that the additional H atom (H1N) in the  $[Hdpo]^+$  cation is shared by the two pyridyl N atoms with identical  $N\cdots H$  distances, suggesting a symmetrical intramolecular  $N\cdots H\cdots N$  hydrogen bond (Table 2). Nearly symmetrical  $N\cdots H\cdots N$  hydrogen bonds, with differences in the  $N\cdots H$  distances in the range 0.05–0.11 Å, have been reported for several pyridinium–pyridine systems (Bock

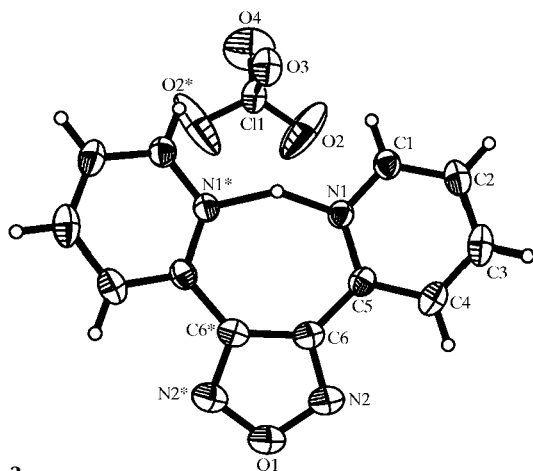


**Figure 1**  
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 25% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms marked with an asterisk (\*) and unlabelled non-H atoms are at the symmetry position ( $-x, -y, z$ ).



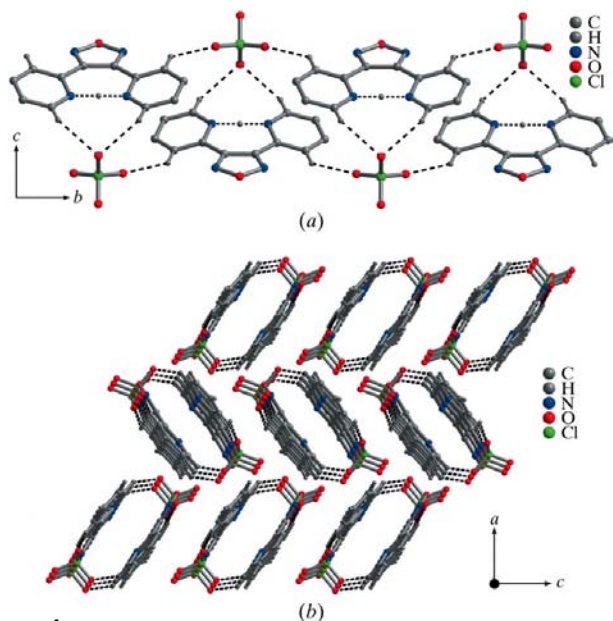
**Figure 2**  
Short contacts around a molecule of (I). H atoms not involved in hydrogen bonding have been omitted for clarity.

*et al.*, 1992; Amoedo-Portela *et al.*, 2002; Wang *et al.*, 2003; Alfonso *et al.*, 2001; Brammer & Zhao, 1995; Fu *et al.*, 2004). Symmetrical hydrogen bonds have also been recognized for neutral  $O \cdots H \cdots O$  (*e.g.* Cheng & Lin, 2006; Macdonald *et al.*, 1972). The  $[Hdpo]^+$  cation is bisected by a crystallographic mirror plane that passes through atoms O1 and H1N. We note that the planarity of  $[Hdpo]^+$  is significantly improved compared with that of the neutral dpo molecule, due to the formation of the intramolecular  $N \cdots H \cdots N$  hydrogen bond; the dihedral angle between the oxadiazole ring and the pyridyl ring is  $12.8(3)^\circ$  and that between the two pyridyl rings is  $19.9(2)^\circ$ .



**Figure 3**

The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms marked with an asterisk (\*) and unlabelled non-H atoms are at the symmetry position  $(x, -y + \frac{1}{2}, z)$ .



**Figure 4**

(a) The one-dimensional tube-like motif in (II), showing the hydrogen bonds and  $\pi$ - $\pi$  interactions (dashed lines) along the  $b$  direction. (b) The packing of the tube-like motifs. H atoms not involved in hydrogen bonding have been omitted for clarity.

As expected, the supramolecular structure of  $[Hdpo]ClO_4$  is distinct from that of dpo. As shown in Fig. 4(a), each  $[Hdpo]^+$  cation is linked to three perchlorate anions through four  $C-H \cdots O$  hydrogen bonds (Table 2) and each perchlorate anion is linked to three  $[Hdpo]^+$  cations. This leads to hydrogen-bonded supramolecular tubes parallel to the  $b$  direction (Fig. 4b). The tube is further stabilized by  $\pi$ - $\pi$  stacking interactions involving two neighbouring pyridyl rings [at  $(x, y, z)$  and  $(1-x, 1-y, 1-z)$ ] from different  $[Hdpo]^+$  cations. The interacting rings are parallel, with a centre-to-centre separation of  $3.66 \text{ \AA}$  and an interplanar separation of  $3.48 \text{ \AA}$  (Fig. 4a).

## Experimental

Dpo was synthesized according to the literature procedure of Richardson *et al.* (2002). Single crystals were obtained by recrystallization from petroleum ether–ethyl acetate (3:1 *v/v*). Crystals of  $[Hdpo]ClO_4$  were prepared by slow evaporation of an ethanol solution of dpo and  $HClO_4$ .

### Compound (I)

#### Crystal data

$C_{12}H_8N_4O$   
 $M_r = 224.22$   
 Orthorhombic,  $Fdd2$   
 $a = 13.0702(8) \text{ \AA}$   
 $b = 21.8905(16) \text{ \AA}$   
 $c = 7.7957(5) \text{ \AA}$   
 $V = 2230.5(3) \text{ \AA}^3$

$Z = 8$   
 $D_x = 1.335 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.09 \text{ mm}^{-1}$   
 $T = 293(2) \text{ K}$   
 Rod, colourless  
 $0.3 \times 0.2 \times 0.2 \text{ mm}$

#### Data collection

Nonius KappaCCD area-detector  
 diffractometer  
 $\varphi$  and  $\omega$  scans  
 8433 measured reflections

676 independent reflections  
 398 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.093$   
 $\theta_{max} = 27.4^\circ$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.065$   
 $wR(F^2) = 0.083$   
 $S = 1.10$   
 676 reflections  
 79 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0334P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.13 \text{ e \AA}^{-3}$   
 $\Delta\rho_{min} = -0.17 \text{ e \AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 (Sheldrick, 1997a)  
 Extinction coefficient:  $0.0037(6)$

**Table 1**

Short-contact geometry ( $\text{\AA}$ ,  $^\circ$ ) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C3-H3A \cdots O1^i$	0.93	2.63	3.379 (4)	139
$C4-H4A \cdots N1^{ii}$	0.93	2.76	3.467 (3)	133

Symmetry codes: (i)  $x + \frac{1}{4}, -y + \frac{1}{4}, z - \frac{3}{4}$ ; (ii)  $-x + \frac{1}{4}, y + \frac{1}{4}, z + \frac{1}{4}$ .

### Compound (II)

#### Crystal data

$C_{12}H_9N_4O^+ \cdot ClO_4^-$   
 $M_r = 324.68$   
 Orthorhombic,  $Pnma$   
 $a = 13.5254(4) \text{ \AA}$   
 $b = 13.1646(4) \text{ \AA}$   
 $c = 7.6908(2) \text{ \AA}$   
 $V = 1369.40(7) \text{ \AA}^3$

$Z = 4$   
 $D_x = 1.575 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.31 \text{ mm}^{-1}$   
 $T = 293(2) \text{ K}$   
 Rod, colourless  
 $0.2 \times 0.1 \times 0.1 \text{ mm}$

## Data collection

Nonius KappaCCD area-detector diffractometer	1631 independent reflections
$\varphi$ and $\omega$ scans	905 reflections with $I > 2\sigma(I)$
21299 measured reflections	$R_{\text{int}} = 0.088$
	$\theta_{\text{max}} = 27.5^\circ$

## Refinement

Refinement on $F^2$	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.064$	
$wR(F^2) = 0.221$	$w = 1/[\sigma^2(F_o^2) + (0.1422P)^2]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
1631 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
109 parameters	$\Delta\rho_{\text{max}} = 0.79 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.56 \text{ e } \text{\AA}^{-3}$

Table 2

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1N\cdots N1^i$	1.382 (19)	1.382 (19)	2.625 (5)	143 (5)
$C1-H1A\cdots O3$	0.93	2.54	3.281 (4)	137
$C4-H4A\cdots O2^{ii}$	0.93	2.46	3.209 (5)	137

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

All H atoms attached to C atoms were placed in calculated positions and refined using a riding model. The H atom involved in  $N\cdots H\cdots N$  hydrogen bonding in (II) was located in a difference map and refined isotropically. The absolute structure of (I) was not determined; because the compound is a weak anomalous scatterer (no atom heavier than Si), Friedel pairs were merged (MERG 4) before the final refinement.

For both compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *maXus* (Mackay *et al.*, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3049). Services for accessing these data are described at the back of the journal.

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