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1,2-Di-4-pyridylethane *N*,*N*′-dioxide–acetic acid (1/2)

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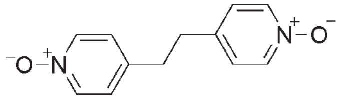
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.001 Å; R factor = 0.044; wR factor = 0.133; data-to-parameter ratio = 21.5.

The title compound, $C_{12}H_{12}N_2O_2·2C_2H_4O_2$, was prepared from 1,2-di-4-pyridylethane, acetic acid, and hydrogen peroxide. The 1,2-di-4-pyridylethane *N*,*N*′-dioxide molecule is located on an inversion center. π–π stacking interactions between neighboring 1,2-di-4-pyridylethane *N*,*N*′-dioxide molecules are observed with a centroid–centroid distance of 3.613 Å, an interplanar distance of 3.317 Å, and a slippage of 1.433 Å. O—H···O hydrogen-bonding interactions between 1,2-di-4-pyridylethane *N*,*N*′-dioxide and acetic acid molecules result in distinct hydrogen-bonded units made of one *N*-oxide and two acetic acid molecules. These units are then linked into a three-dimensional network through weaker C—H···O hydrogen-bonding interactions.

Related literature

For the synthesis of 2,2′-bipyridine *N*,*N*′-dioxide, see: Simpson *et al.* (1963). For the synthesis of 1,2-di-4-pyridylethane *N*,*N*′-dioxide peroxide disolvate and its use in the synthesis of lanthanide coordination networks, see: Lu *et al.* (2002). Zhang, Du *et al.* (2004) and Zhang, Lu *et al.* (2004) also report the use of 1,2-di-4-pyridylethane *N*,*N*′-dioxide in the preparation of lanthanide coordination networks.



·2(CH_3COOH)

Experimental

Crystal data

$C_{12}H_{12}N_2O_2·2C_2H_4O_2$
M_r = 336.34
Triclinic, $P\bar{1}$
a = 7.1109 (6) Å
b = 7.1562 (6) Å
c = 9.2888 (7) Å
α = 73.719 (1)°
β = 87.508 (1)°
γ = 64.424 (1)°
V = 407.62 (6) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 173 K
0.55 × 0.45 × 0.37 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001) T_{min} = 0.944, T_{max} = 0.962
4857 measured reflections
2446 independent reflections
2228 reflections with $I > 2\sigma(I)$
R_{int} = 0.011

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.133
S = 1.09
2446 reflections
114 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1^{i}	0.84	1.72	2.5393 (11)	164
C1—H1···O2^{i}	0.95	2.68	3.3915 (12)	132
C2—H2···O3^{ii}	0.95	2.45	3.3489 (11)	158
C5—H5···O1^{iii}	0.95	2.48	3.3341 (12)	149
C6—H6*B*···O1^{iv}	0.99	2.66	3.6309 (12)	168
C8—H8*C*···O1^{v}	0.98	2.52	3.3655 (13)	145

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

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *X-SEED*.

The authors are grateful to Allegheny College for providing funding in support of this research. The diffractometer was funded by the NSF (grant No. 0087210), the Ohio Board of Regents (grant No. CAP-491) and by Youngstown State University. The authors would also like to acknowledge the STaRBURSTT CyberInstrumentation Consortium for assistance with the crystallography.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2243).

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supplementary materials

Acta Cryst. (2009). E**65**, o2970 [**doi:10.1107/S1600536809044912**]

1,2-Di-4-pyridylethane *N*,*N*'-dioxide-acetic acid (1/2)

E. P. Boron and **J. M. Knaust**

Comment

The use of aromatic *N*,*N*'-dioxide ligands in the synthesis of coordination networks has been of recent interest (Lu *et al.* (2002), Zhang, Du *et al.* (2004) and Zhang, Lu *et al.* (2004)). The title compound was prepared using the reaction conditions described by Simpson *et al.* (1963) to prepare 2,2'-bipyridine *N*,*N*'-dioxide. The molar ratios of reactants used to form the title compound were 1:20:3 (1,2-di-4-pyridylethane, acetic acid, and peroxide), and the reaction mixture was heated for 21 h. However, when precipitation of the product did not occur following the addition of acetone as described by Simpson *et al.* (1963), the solution was cooled to 273 K, and crystals of the title compound slowly formed. Lu *et al.* (2002) described the synthesis of 1,2-di-4-pyridylethane *N*,*N*'-dioxide peroxide disolvate using a slightly modified version of the conditions described by Simpson *et al.* (1963). The molar ratios of reactants used by Lu *et al.* (2002) are 1:13:8, and the reaction was heated for 12 h. Lu *et al.* (2002) removed all excess acetic acid and water under vacuum before adding acetone to the resulting oil to precipitate the crude product; the crude product was washed to remove unreacted 1,2-di-4-pyridylethane and recrystallized to give 1,2-di-4-pyridylethane *N*,*N*'-dioxide peroxide disolvate. Presumably, the formation of the acetic acid adduct *versus* the peroxide adduct is due to the difference in reaction and crystallization conditions. The title compound is formed with a high 1,2-di-4-pyridylethane to acetic acid ratio and crystallization directly from the reaction solution. Whereas the peroxide adduct is formed with a high 1,2-di-4-pyridylethane to peroxide ratio and removal of excess acetic acid before crystallization.

The asymmetric unit of the title compound contains half of a 1,2-di-4-pyridylethane *N*,*N*'-dioxide molecule and one acetic acid molecule (Figure 1). The 1,2-di-4-pyridylethane *N*,*N*'-dioxide sits on a center of inversion. π-π stacking interactions with a centroid to centroid distance of 3.6133 Å, an interplanar distance of 3.3171 Å, and a slippage of 1.433 Å. are observed between neighboring N-oxide molecules [symmetry code: $-x + 1$, $-y + 1$, $-z$] (Figure 2). The title compound forms distinct O—H···O hydrogen bonded units made of one N-oxide molecule and two acetic acid molecules (Figure 3). Weaker O—H···O hydrogen bonding interactions are also observed between N-oxide and acetic acid molecules and between neighboring N-oxide molecules (Figure 4). As seen in the packing diagram, the N-oxide and acetic acid molecules are linked into a three-dimensional hydrogen-bonding network (Figure 5).

Experimental

1,2-Di-4-pyridylethane (11.7918 g, 64.0 mmol), acetic acid (75 ml), and 35% hydrogen peroxide (11.1 ml) were heated at 343–353K (70–80 °C) for 3 h. Additional hydrogen peroxide (7.8 ml) was added, and heating was continued. After an additional 19 h of heating the solution was cooled to room temperature. Crystals formed upon the addition of acetone (1*L*) and cooling to 273 K.

Refinement

All H atoms were positioned geometrically and refined using a riding model with C—H = 0.95–0.99 Å and with U_{iso}(H) = 1.2 (1.5 for methyl groups) times U_{eq}(C), and O—H = 0.84 Å and U_{iso}(H) = 1.5 times U_{eq}(O).

Figures

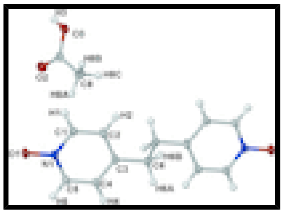

Fig. 1. The molecular structure of the title compound with atom labels and 50% probability displacement ellipsoids for non-H atoms.

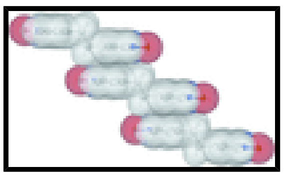

Fig. 2. π-π interactions between neighboring 1,2-di-4-pyridylethane *N*,*N*'-dioxide molecules.

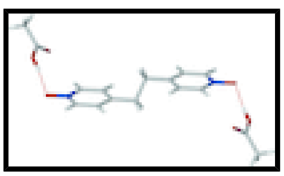

Fig. 3. O—H···O hydrogen bonded units made of one 1,2-di-4-pyridylethane *N*,*N*'-dioxide molecule and two acetic acid molecules. Hydrogen bonds are shown as dashed lines.

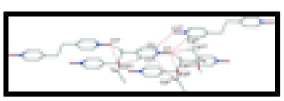

Fig. 4. O—H···O and C—H···O hydrogen bonding interactions between 1,2-di-4-pyridylethane *N*,*N*'-dioxide and neighboring 1,2-di-4-pyridylethane *N*,*N*'-dioxide and acetic acid molecules. Hydrogen bonds are shown as dashed lines. Hydrogen atoms not involved in the hydrogen bonds shown have been omitted for clarity. Symmetry codes: (ii) -*x* + 1, -*y* + 2, -*z* + 1; (iii) -*x* + 2, -*y* + 1, -*z* + 1; (iv) -*x*, -*y* + 2, -*z*; (v) *x* + 1, *y* - 1, *z*; (vii) *x* - 1, *y*, *z*; (viii) *x* - 1,*y* + 1, *z*.

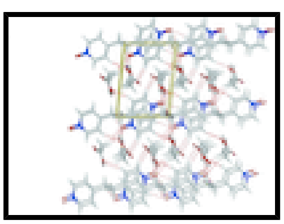

Fig. 5. Packing of the title compound viewed down the *b* axis. Hydrogen bonds are shown as dashed lines.

1,2-Di-4-pyridylethane *N*,*N*'-dioxide–acetic acid (1/2)

Crystal data

$C_{12}H_{12}N_2O_2·2C_2H_4O_2$	Z = 1
M_r = 336.34	F_{000} = 178
Triclinic, $P\bar{1}$	D_x = 1.370 Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 7.1109 (6) Å	Cell parameters from 3794 reflections
b = 7.1562 (6) Å	θ = 3.2–30.5°

c = 9.2888 (7) Å	μ = 0.11 mm^{-1}
α = 73.719 (1)°	T = 173 K
β = 87.508 (1)°	Block, colorless
γ = 64.424 (1)°	0.55 × 0.45 × 0.37 mm
V = 407.62 (6) Å^3	

Data collection

Bruker SMART APEX CCD diffractometer	2446 independent reflections
Radiation source: fine-focus sealed tube	2228 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.011
T = 173 K	θ_{max} = 30.5°
ω scans	θ_{min} = 2.3°
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$h = -10 \rightarrow 10$
T_{min} = 0.944, T_{max} = 0.962	$k = -10 \rightarrow 9$
4857 measured reflections	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.044	H-atom parameters constrained
$wR(F^2)$ = 0.133	$w = 1/[\sigma^2(F_o^2) + (0.0796P)^2 + 0.0824P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.09	$(\Delta/\sigma)_{max}$ = 0.001
2446 reflections	$\Delta\rho_{max}$ = 0.39 e Å^{-3}
114 parameters	$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}

O1	0.13750 (10)	0.89616 (12)	0.18453 (8)	0.02574 (15)
O2	0.65037 (13)	1.15878 (12)	0.46617 (9)	0.03371 (18)
O3	0.86230 (12)	0.87364 (12)	0.65134 (8)	0.02891 (16)
H3	0.8470	0.9693	0.6925	0.043*
N1	0.32388 (11)	0.79711 (12)	0.13545 (9)	0.019
C1	0.48607 (14)	0.64120 (15)	0.23478 (10)	0.022
H1	0.4674	0.6045	0.3391	0.026*
C2	0.67866 (13)	0.53522 (15)	0.18518 (10)	0.02148 (17)
H2	0.7919	0.4267	0.2558	0.026*
C3	0.70835 (13)	0.58611 (14)	0.03222 (10)	0.01794 (15)
C4	0.53728 (13)	0.74729 (14)	−0.06672 (10)	0.01899 (16)
H4	0.5520	0.7860	−0.1717	0.023*
C5	0.34614 (13)	0.85159 (14)	−0.01355 (10)	0.01970 (16)
H5	0.2308	0.9614	−0.0819	0.024*
C6	0.91767 (13)	0.46745 (14)	−0.02202 (10)	0.01940 (16)
H6A	0.9022	0.5004	−0.1329	0.023*
H6B	0.9662	0.3095	0.0222	0.023*
C7	0.76154 (14)	0.96654 (16)	0.51521 (10)	0.02359 (18)
C8	0.80145 (17)	0.80587 (18)	0.42910 (12)	0.0301 (2)
H8A	0.6925	0.8686	0.3456	0.045*
H8B	0.7993	0.6741	0.4963	0.045*
H8C	0.9386	0.7700	0.3892	0.045*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0129 (3)	0.0322 (4)	0.0298 (3)	−0.0051 (3)	0.0056 (2)	−0.0140 (3)
O2	0.0348 (4)	0.0244 (4)	0.0278 (4)	−0.0039 (3)	0.0014 (3)	−0.0014 (3)
O3	0.0253 (3)	0.0244 (3)	0.0276 (4)	−0.0027 (3)	−0.0033 (3)	−0.0063 (3)
N1	0.012	0.020	0.024	−0.005	0.003	−0.008
C1	0.017	0.024	0.021	−0.006	0.001	−0.006
C2	0.0149 (4)	0.0216 (4)	0.0235 (4)	−0.0041 (3)	0.0004 (3)	−0.0061 (3)
C3	0.0131 (3)	0.0171 (4)	0.0241 (4)	−0.0063 (3)	0.0025 (3)	−0.0073 (3)
C4	0.0157 (4)	0.0184 (4)	0.0214 (4)	−0.0069 (3)	0.0024 (3)	−0.0046 (3)
C5	0.0148 (3)	0.0184 (4)	0.0233 (4)	−0.0056 (3)	0.0010 (3)	−0.0047 (3)
C6	0.0136 (3)	0.0195 (4)	0.0260 (4)	−0.0064 (3)	0.0038 (3)	−0.0096 (3)
C7	0.0177 (4)	0.0260 (4)	0.0224 (4)	−0.0078 (3)	0.0058 (3)	−0.0036 (3)
C8	0.0292 (5)	0.0314 (5)	0.0272 (5)	−0.0109 (4)	0.0061 (4)	−0.0093 (4)

Geometric parameters (Å, °)

O1—N1	1.3358 (9)	C3—C6	1.5079 (11)
O2—C7	1.2107 (12)	C4—C5	1.3859 (11)
O3—C7	1.3231 (12)	C4—H4	0.9500
O3—H3	0.8400	C5—H5	0.9500
N1—C5	1.3506 (12)	C6—C6^{i}	1.5410 (17)
N1—C1	1.3530 (12)	C6—H6A	0.9900
C1—C2	1.3811 (12)	C6—H6B	0.9900

C1—H1	0.9500	C7—C8	1.5021 (14)
C2—C3	1.3950 (13)	C8—H8A	0.9800
C2—H2	0.9500	C8—H8B	0.9800
C3—C4	1.3951 (12)	C8—H8C	0.9800
O1—N1—C1	119.76 (8)	C1—C2—H2	119.7
C5—N1—C1	120.99 (8)	C2—C1—H1	119.8
O1—N1—C5	119.24 (7)	C3—C2—H2	119.7
N1—C1—C2	120.31 (8)	C3—C4—H4	119.6
N1—C5—C4	120.00 (8)	C3—C6—H6A	109.3
C1—C2—C3	120.58 (8)	C3—C6—H6B	109.3
C2—C3—C4	117.43 (8)	C4—C5—H5	120.0
C3—C4—C5	120.70 (8)	C5—C4—H4	119.6
C4—C3—C6	122.07 (8)	C6^{i}—C6—H6A	109.3
C2—C3—C6	120.50 (8)	C6^{i}—C6—H6B	109.3
C3—C6—C6^{i}	111.43 (8)	C7—C8—H8A	109.5
O2—C7—O3	123.73 (10)	C7—C8—H8B	109.5
O2—C7—C8	124.14 (9)	C7—C8—H8C	109.5
O3—C7—C8	112.13 (8)	H6A—C6—H6B	108.0
N1—C1—H1	119.8	H8A—C8—H8B	109.5
N1—C5—H5	120.0	H8A—C8—H8C	109.5
C7—O3—H3	109.5	H8B—C8—H8C	109.5

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O1^{ii}	0.84	1.72	2.5393 (11)	164
C1—H1···O2^{ii}	0.95	2.68	3.3915 (12)	132
C2—H2···O3^{iii}	0.95	2.45	3.3489 (11)	158
C5—H5···O1^{iv}	0.95	2.48	3.3341 (12)	149
C6—H6B···O1^{v}	0.99	2.66	3.6309 (12)	168
C8—H8C···O1^{vi}	0.98	2.52	3.3655 (13)	145

Symmetry codes: (ii) −*x*+1, −*y*+2, −*z*+1; (iii) −*x*+2, −*y*+1, −*z*+1; (iv) −*x*, −*y*+2, −*z*; (v) *x*+1, *y*−1, *z*; (vi) *x*+1, *y*, *z*.

Fig. 1

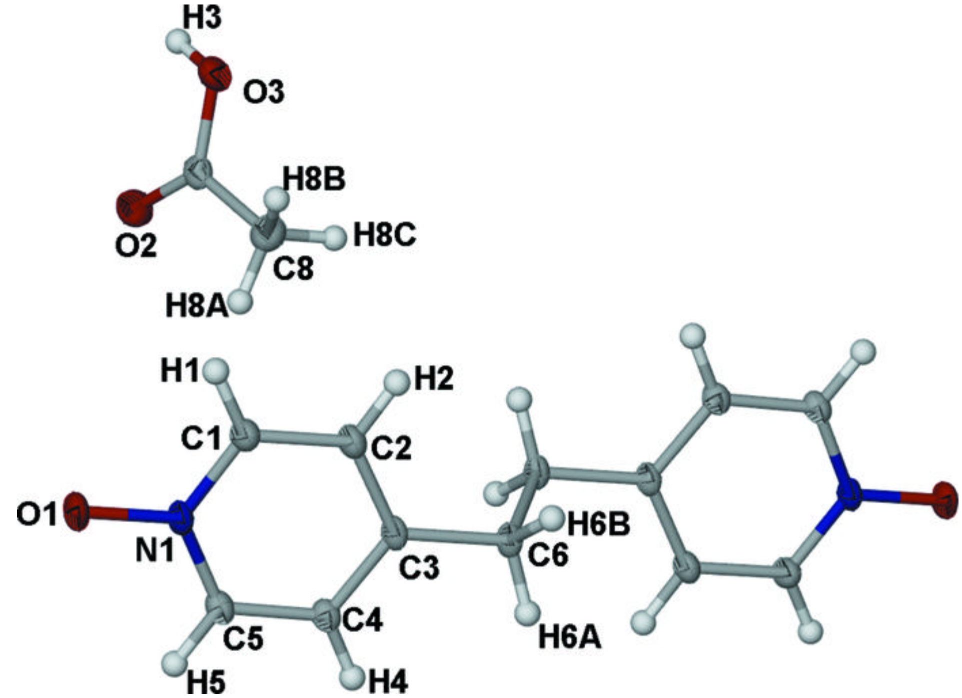

Fig. 2

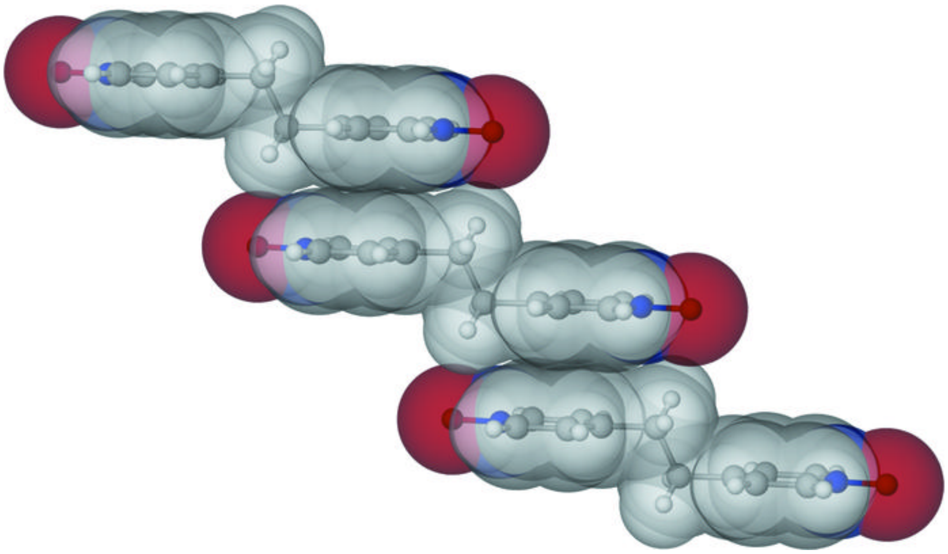

Fig. 3

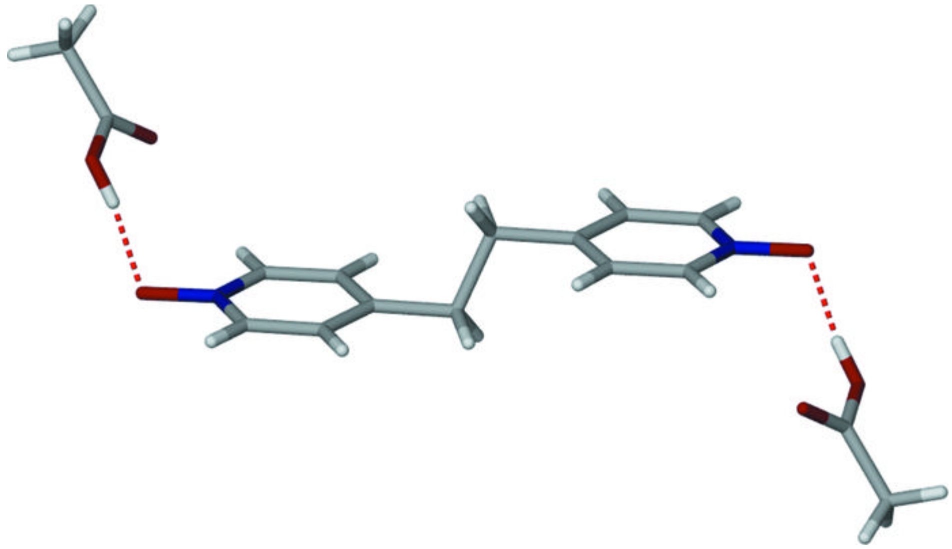

Fig. 4

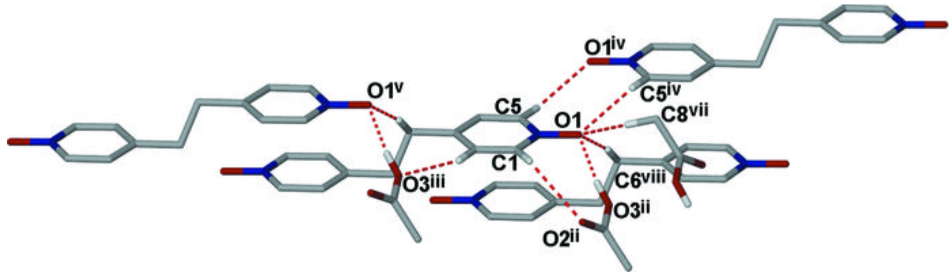

Fig. 5