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(*E*)-3-(2-Nitriminoimidazolidin-1-yl)-1-phenylpropan-1-one

Haibo Yu, Bingnan Zhang and Jianxin Fang*

State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China
Correspondence e-mail: yssfjx@yahoo.com.cn

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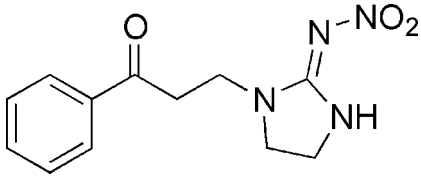
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.003 Å; R factor = 0.044; wR factor = 0.135; data-to-parameter ratio = 14.9.

In the crystal structure of the title compound, $C_{12}H_{14}N_4O_3$, the dihedral angle between the phenyl and imidazole rings is 76.55 (7)°. The nitrite O atoms of the (*E*)-2-nitriminoimidazolidin-1-yl group act as the acceptors of three N—H···O hydrogen bonds from the N atom of the imidazole ring, resulting in a one-dimensional chain. C—H···O hydrogen-bonding interactions are also observed in this complex, extending the structure into a two-dimensional supramolecular sheet.

Related literature

For related literature, see: Etter (1990); Kagabu (1999); Yamamoto (1996); Yamamoto & Casida (1999).



Experimental

Crystal data

$C_{12}H_{14}N_4O_3$
M_r = 262.27
Monoclinic, $P2_1/c$
a = 15.346 (4) Å
b = 6.0908 (15) Å
c = 13.784 (3) Å
β = 102.098 (4)°
V = 1259.8 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 294 (2) K
0.28 × 0.24 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.972, T_{max} = 0.980
6913 measured reflections
2582 independent reflections
1534 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.135
S = 1.00
2582 reflections
173 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O2^{i}	0.86	2.60	3.272 (3)	136
N2—H2···O3^{i}	0.86	2.49	3.260 (3)	150
C9—H9*B*···O2^{ii}	0.97	2.50	3.314 (3)	141
N2—H2···O3	0.86	2.11	2.605 (3)	116
C9—H9*A*···N3	0.97	2.42	2.814 (2)	104

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2297).

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  doi:10.1107/S1600536807047939

supplementary materials

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(*E*)-3-(2-Nitriminoimidazolidin-1-yl)-1-phenylpropan-1-one

H. Yu, B. Zhang and J. Fang

Comment

Neonicotinoids (Yamamoto, 1996) represent a novel and distinct chemical class of insecticides with remarkable chemical and biological properties (Yamamoto Casida, 1999), which hold low degree of toxicity to mammals and aquatic life, and stability in the fields. Neonicotinoids act at the acetylcholine binding site of the nicotinic acetylcholine receptor (nAChR) of insects and the nitroimino imidazolidine is an important pharmcophore. Kagabu proposed that the nitrogen atom at the 1-position of the imidazolidine ring and one of the oxygen atoms of the nitro group play an important role in the interaction with the binding sites on nAChR (Kagabu, 1999).

The molecular structure of (I) (Fig. 1) contains no crystallographically imposed symmetry. The imidazole and benzene rings in each of the ligands are not coplanar, the dihedral angle formed by the least-squares planes of the phenyl and imidazole rings being equal to 76.55 (7)°. The dihedral angles between the mean plane of the imidazole ring and the plane of the N4/O2/O3 group are 4.67 (15)°. Selected bond lengths and angles are listed in Table 1.

Analysis of the crystal packing of (I) shows the existence of three N—H···O (two intermolecular and one intramolecular) interactions between the nitrite O atoms of the *L* ligand and the imidazole N atom, resulting in a one-dimensional chain along with [001] direction, as shown in Fig. 2. In this 1-D chain, a hydrogen-bonded ring, N = $R^2(3)$, is generated (Etter, 1990), which comprises one imidazole N2 atom and two O atoms of the nitrite group (O2 and O3). Furthermore, this 1-D chains are extended into 2-D supramolecular sheet *via* C(9)—H(B)···O(2) hydrogen bonds in *bc* plane [Symmetry code: *x*, 3/2 − *y*, 1/2 + *z*], as shown in Fig. 3. A significant intramolecular C(9)—H(9 A)···N(3) interaction is also observed, which contributes strongly to the stability of the structure. All relevant hydrogen-bonding geometries are listed in Table 2.

Experimental

A suspension of 3-choro-1-phenylpropan-1-one (1.68 g, 10 mmol), nitroimino imidazolidine (1.31 g, 10 mmol) and potassium carbonate (1.38 g, 10 mmol) in 25 ml of methyl cyanide was heated to reflux for 30 min. The reaction was quenched with water and extracted with methylene chloride. The extract was washed with brine, dried over anhydrous magnesium sulfate and the solvent evaporated. The residue was purified by silica gel column chromatography to give the target compound. The crystal was grown by slow evaporation of an ethanol solution at room temperature. Anal. Calcd for $C_{12}H_{14}N_4O_3$: C, 55.90; H, 5.63; N, 8.69. Found: C, 55.67; H, 5.64; N, 8.66. ^{1}H NMR ($CDCl_3$): 3.372 (b, 2H, CH_2), 3.775 (s, 6H, –NCH_2N–), 7.465–7.551 (m, 2H, Ar—H), 7.623–7.579 (m, 1H, Ar—H), 7.660 (dd, 2H, Ar—H), 8.020 (s, 1H, NH).

Refinement

Although all H atoms were visible in difference maps, they were placed in geometrically calculated positions, with C—H distances in the range 0.93–0.97 Å and N—H distances of 0.86 Å, and included in the final refinement in the riding model approximation,with U_{iso}(H) = 1.2U_{eq}(C) for aromatic and methylene H atoms.

Figures

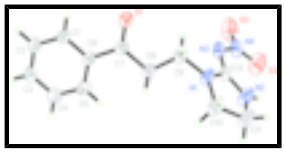

Fig. 1. The molecular structure of (I), with atom labels and 30% probability displacement ellipsoids.

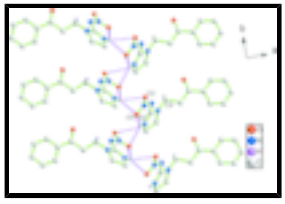

Fig. 2. The packing of (I), viewed down the *b* axis, showing one-dimensional chain connected by C—H···N hydrogen bonds (dashed lines). H atoms not involved in hydrogen bonding have been omitted. [Symmetry code: (i) $1-x$, $1/2+y$, $1/2-z$; (ii) x, $3/2-y$, $1/2+z$].

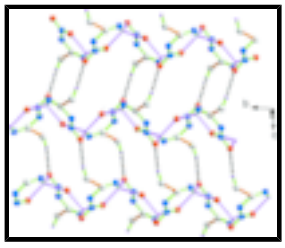

Fig. 3. A view of the two-dimensional supramolecular sheet of (I), showing the C—H···O hydrogen-bonding interactions (black dashed lines). The *L* molecules have been partly omitted for clarity.

(*E*)-3-(2-Nitriminoimidazolidin-1-yl)-1-phenylpropan-1-one

Crystal data

$C_{12}H_{14}N_4O_3$	F_{000} = 552
M_r = 262.27	D_x = 1.383 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 1967 reflections
a = 15.346 (4) Å	θ = 2.7–26.2°
b = 6.0908 (15) Å	μ = 0.10 mm^{-1}
c = 13.784 (3) Å	T = 294 (2) K
β = 102.098 (4)°	Block, colourless
V = 1259.8 (5) Å^3	0.28 × 0.24 × 0.20 mm
Z = 4	

Data collection

Bruker SMART CCD area-detector diffractometer	2582 independent reflections
Radiation source: fine-focus sealed tube	1534 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.039
T = 294(2) K	θ_{max} = 26.4°
φ and ω scans	θ_{min} = 1.4°
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −18→19
T_{min} = 0.972, T_{max} = 0.980	k = −6→7

6913 measured reflections

$l = -17 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.135$

$S = 1.00$

2582 reflections

173 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2 + 0.2621P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.17$ e Å^{-3}

$\Delta\rho_{min} = -0.19$ e Å^{-3}

Extinction correction: SHELXL97 (Sheldrick, 1997)

Extinction coefficient: 0.015 (3)

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 $F^2 > 2$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	0.89456 (9)	0.4085 (3)	0.57018 (12)	0.0741 (5)
O2	0.62133 (12)	0.2316 (4)	0.85036 (15)	0.1197 (8)
O3	0.54319 (14)	−0.0283 (4)	0.77931 (16)	0.1252 (8)
N1	0.68641 (11)	−0.0235 (3)	0.57030 (13)	0.0690 (5)
N2	0.58391 (13)	−0.2046 (4)	0.62248 (17)	0.0955 (7)
H2	0.5493	−0.2437	0.6611	0.115*
N3	0.65419 (10)	0.1137 (3)	0.71315 (13)	0.0668 (5)
N4	0.60406 (13)	0.1005 (4)	0.78249 (15)	0.0814 (6)
C1	1.07620 (13)	0.3262 (3)	0.62309 (14)	0.0575 (5)
H1	1.0577	0.4668	0.6018	0.069*
C2	1.16612 (14)	0.2813 (4)	0.65379 (16)	0.0666 (6)
H2A	1.2078	0.3920	0.6533	0.080*
C3	1.19427 (14)	0.0738 (4)	0.68500 (15)	0.0670 (6)
H3	1.2547	0.0448	0.7069	0.080*
C4	1.13284 (14)	−0.0900 (4)	0.68366 (16)	0.0694 (6)
H4	1.1519	−0.2313	0.7031	0.083*

C5	1.04285 (14)	−0.0474 (4)	0.65363 (15)	0.0613 (6)
H5	1.0018	−0.1597	0.6534	0.074*
C6	1.01342 (12)	0.1622 (3)	0.62384 (12)	0.0483 (5)
C7	0.91721 (13)	0.2204 (3)	0.59318 (13)	0.0528 (5)
C8	0.84777 (12)	0.0457 (3)	0.59221 (14)	0.0560 (5)
H8A	0.8564	−0.0212	0.6574	0.067*
H8B	0.8550	−0.0676	0.5451	0.067*
C9	0.75451 (12)	0.1381 (4)	0.56442 (15)	0.0630 (6)
H9A	0.7491	0.2595	0.6083	0.076*
H9B	0.7446	0.1951	0.4973	0.076*
C10	0.66626 (17)	−0.2033 (5)	0.5001 (2)	0.0954 (9)
H10A	0.7167	−0.3017	0.5055	0.114*
H10B	0.6496	−0.1494	0.4326	0.114*
C11	0.58803 (18)	−0.3171 (5)	0.5314 (2)	0.1044 (10)
H11A	0.5334	−0.2981	0.4821	0.125*
H11B	0.5994	−0.4727	0.5427	0.125*
C12	0.63860 (12)	−0.0357 (4)	0.64033 (16)	0.0596 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0635 (9)	0.0647 (10)	0.0971 (12)	−0.0063 (8)	0.0236 (8)	0.0197 (8)
O2	0.0866 (13)	0.189 (2)	0.0880 (13)	−0.0068 (14)	0.0296 (10)	−0.0507 (15)
O3	0.1108 (15)	0.163 (2)	0.1241 (17)	−0.0436 (16)	0.0761 (13)	−0.0316 (15)
N1	0.0608 (10)	0.0798 (13)	0.0744 (12)	−0.0253 (9)	0.0326 (9)	−0.0172 (10)
N2	0.0827 (14)	0.1091 (17)	0.1117 (17)	−0.0450 (13)	0.0591 (12)	−0.0252 (14)
N3	0.0461 (9)	0.0920 (14)	0.0656 (11)	−0.0005 (9)	0.0192 (8)	−0.0066 (10)
N4	0.0522 (11)	0.1243 (19)	0.0696 (13)	0.0040 (12)	0.0174 (9)	−0.0096 (13)
C1	0.0618 (12)	0.0540 (12)	0.0613 (12)	−0.0126 (10)	0.0236 (10)	−0.0065 (9)
C2	0.0551 (13)	0.0727 (15)	0.0761 (15)	−0.0174 (11)	0.0232 (11)	−0.0169 (12)
C3	0.0563 (12)	0.0864 (17)	0.0583 (13)	0.0008 (12)	0.0119 (10)	−0.0079 (12)
C4	0.0686 (14)	0.0687 (14)	0.0697 (14)	0.0024 (12)	0.0117 (11)	0.0087 (11)
C5	0.0660 (13)	0.0586 (13)	0.0601 (12)	−0.0130 (10)	0.0148 (10)	0.0075 (10)
C6	0.0539 (11)	0.0547 (12)	0.0395 (10)	−0.0108 (9)	0.0171 (8)	−0.0027 (8)
C7	0.0624 (12)	0.0554 (13)	0.0448 (11)	−0.0102 (10)	0.0207 (9)	0.0042 (9)
C8	0.0558 (11)	0.0613 (13)	0.0538 (11)	−0.0144 (10)	0.0178 (9)	−0.0012 (9)
C9	0.0553 (12)	0.0714 (15)	0.0659 (13)	−0.0175 (10)	0.0210 (10)	−0.0018 (11)
C10	0.0881 (17)	0.105 (2)	0.107 (2)	−0.0444 (16)	0.0515 (15)	−0.0386 (17)
C11	0.0877 (18)	0.113 (2)	0.128 (2)	−0.0473 (17)	0.0580 (17)	−0.0403 (19)
C12	0.0395 (10)	0.0732 (14)	0.0682 (13)	−0.00	0.0164 (9)	0.0008 (11)

Geometric parameters (Å, °)

O1—C7	1.220 (2)	C3—H3	0.9300
O2—N4	1.216 (3)	C4—C5	1.381 (3)
O3—N4	1.214 (3)	C4—H4	0.9300
N1—C12	1.332 (2)	C5—C6	1.387 (3)
N1—C9	1.450 (2)	C5—H5	0.9300
N1—C10	1.451 (3)	C6—C7	1.491 (3)

N2—C12	1.318 (3)	C7—C8	1.504 (3)
N2—C11	1.443 (3)	C8—C9	1.511 (3)
N2—H2	0.8600	C8—H8A	0.9700
N3—C12	1.338 (3)	C8—H8B	0.9700
N3—N4	1.349 (2)	C9—H9A	0.9700
C1—C2	1.383 (3)	C9—H9B	0.9700
C1—C6	1.390 (2)	C10—C11	1.525 (3)
C1—H1	0.9300	C10—H10A	0.9700
C2—C3	1.375 (3)	C10—H10B	0.9700
C2—H2A	0.9300	C11—H11A	0.9700
C3—C4	1.370 (3)	C11—H11B	0.9700
C12—N1—C9	126.26 (18)	O1—C7—C8	119.96 (18)
C12—N1—C10	111.61 (17)	C6—C7—C8	119.49 (17)
C9—N1—C10	122.04 (16)	C7—C8—C9	111.77 (17)
C12—N2—C11	113.02 (18)	C7—C8—H8A	109.3
C12—N2—H2	123.5	C9—C8—H8A	109.3
C11—N2—H2	123.5	C7—C8—H8B	109.3
C12—N3—N4	116.87 (19)	C9—C8—H8B	109.3
O3—N4—O2	119.6 (2)	H8A—C8—H8B	107.9
O3—N4—N3	124.2 (2)	N1—C9—C8	112.88 (18)
O2—N4—N3	116.2 (2)	N1—C9—H9A	109.0
C2—C1—C6	120.3 (2)	C8—C9—H9A	109.0
C2—C1—H1	119.9	N1—C9—H9B	109.0
C6—C1—H1	119.9	C8—C9—H9B	109.0
C3—C2—C1	120.4 (2)	H9A—C9—H9B	107.8
C3—C2—H2A	119.8	N1—C10—C11	103.03 (19)
C1—C2—H2A	119.8	N1—C10—H10A	111.2
C4—C3—C2	119.7 (2)	C11—C10—H10A	111.2
C4—C3—H3	120.2	N1—C10—H10B	111.2
C2—C3—H3	120.2	C11—C10—H10B	111.2
C3—C4—C5	120.6 (2)	H10A—C10—H10B	109.1
C3—C4—H4	119.7	N2—C11—C10	102.15 (19)
C5—C4—H4	119.7	N2—C11—H11A	111.3
C4—C5—C6	120.34 (19)	C10—C11—H11A	111.3
C4—C5—H5	119.8	N2—C11—H11B	111.3
C6—C5—H5	119.8	C10—C11—H11B	111.3
C5—C6—C1	118.72 (19)	H11A—C11—H11B	109.2
C5—C6—C7	122.99 (17)	N2—C12—N1	109.5 (2)
C1—C6—C7	118.29 (18)	N2—C12—N3	132.64 (19)
O1—C7—C6	120.55 (17)	N1—C12—N3	117.82 (18)
C12—N3—N4—O3	−4.6 (3)	C12—N1—C9—C8	105.8 (2)
C12—N3—N4—O2	177.2 (2)	C10—N1—C9—C8	−70.6 (3)
C6—C1—C2—C3	0.2 (3)	C7—C8—C9—N1	−175.57 (16)
C1—C2—C3—C4	1.3 (3)	C12—N1—C10—C11	6.7 (3)
C2—C3—C4—C5	−1.6 (3)	C9—N1—C10—C11	−176.4 (2)
C3—C4—C5—C6	0.4 (3)	C12—N2—C11—C10	7.1 (3)
C4—C5—C6—C1	1.2 (3)	N1—C10—C11—N2	−7.8 (3)
C4—C5—C6—C7	−178.32 (17)	C11—N2—C12—N1	−3.2 (3)

C2—C1—C6—C5	−1.5 (3)	C11—N2—C12—N3	178.0 (2)
C2—C1—C6—C7	178.05 (16)	C9—N1—C12—N2	−179.2 (2)
C5—C6—C7—O1	177.96 (18)	C10—N1—C12—N2	−2.6 (3)
C1—C6—C7—O1	−1.6 (3)	C9—N1—C12—N3	−0.3 (3)
C5—C6—C7—C8	−1.1 (3)	C10—N1—C12—N3	176.4 (2)
C1—C6—C7—C8	179.35 (16)	N4—N3—C12—N2	−2.3 (4)
O1—C7—C8—C9	−2.1 (3)	N4—N3—C12—N1	178.99 (19)
C6—C7—C8—C9	177.01 (15)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O2^{i}	0.86	2.60	3.272 (3)	136
N2—H2···O3^{i}	0.86	2.49	3.260 (3)	150
C9—H9B···O2^{ii}	0.97	2.50	3.314 (3)	141
N2—H2···O3	0.86	2.11	2.605 (3)	116
C9—H9A···N3	0.97	2.42	2.814 (2)	104

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+3/2; (ii) *x*, −*y*+1/2, *z*−1/2.

Fig. 1

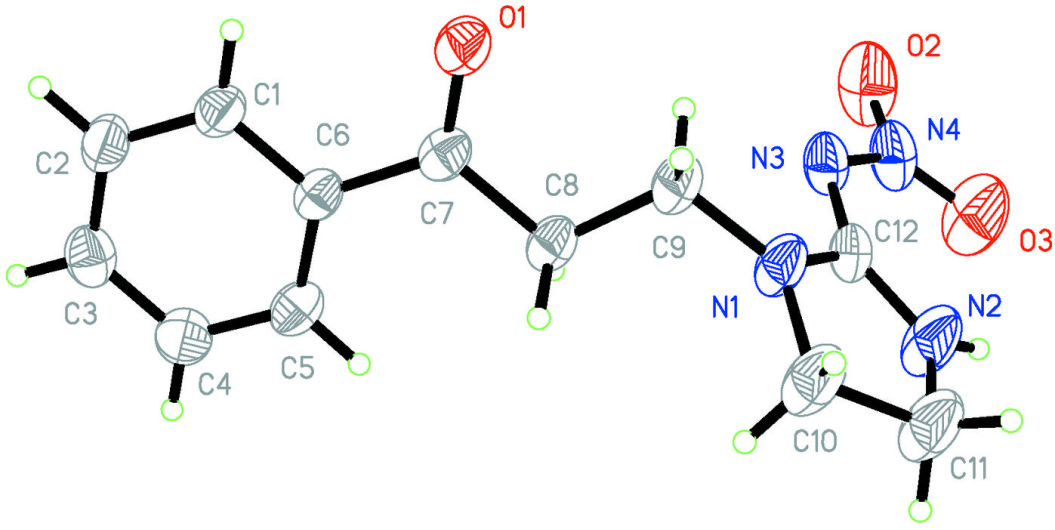

Fig. 2

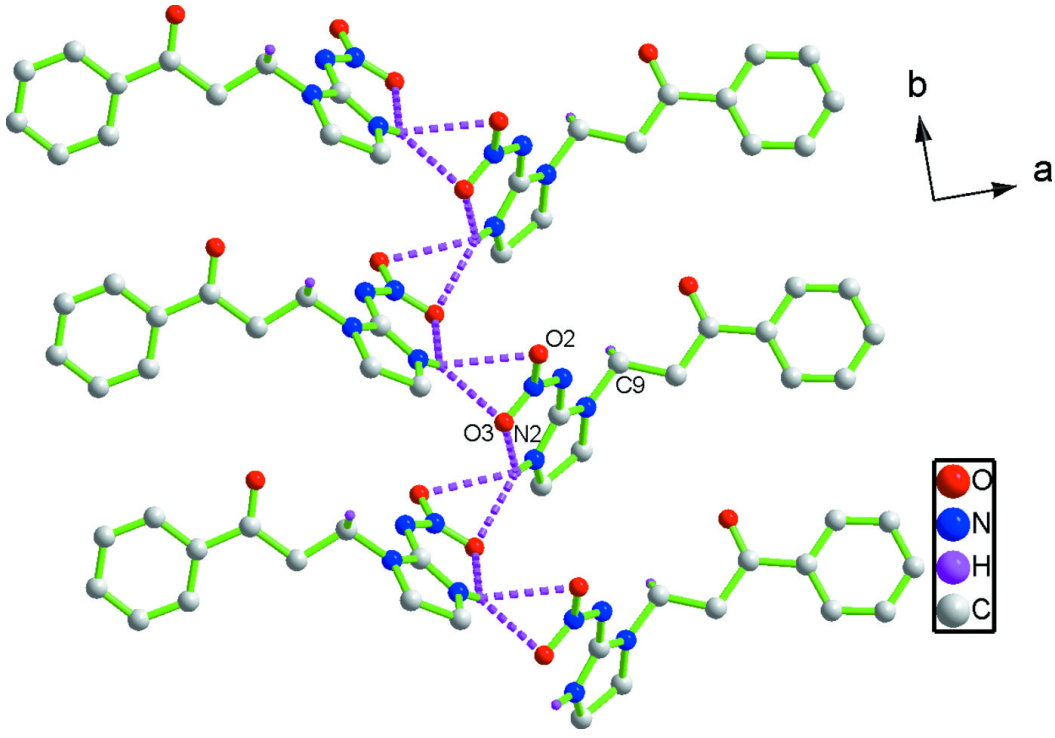

Fig. 3