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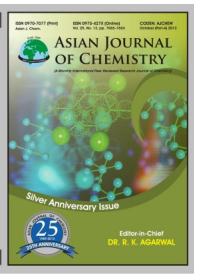

Synthesis, Crystal and Supermolecular Structure of (*Z*)-4-({4-[1-(Hydroxyimino)ethyl]-phenylimino}(phenyl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one

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The compound, (*Z*)-4-({4-[1-(hydroxyimino)ethyl]phenylimino}(phenyl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one has been synthesized and characterized by elemental analyses, IR spectra and X-ray diffraction method. This compound is a potential tridentate ligand containing mono-oxime group. In the crystal structure, there are two crystallographically independent but chemically identical molecules (molecules A and B). There are two strong intramolecular N3-H3···O1 and N7-H7···O3 hydrogen bonds form six-membered S(6) ring motifs. Each molecule A interlinks two neighboring molecules B into a 1D infinite chain through six intermolecular O2-H2···N6, C29-H29A···O2, C35-H35···N4, O4-H4···N2, C4-H4A···O4 and C10-H10···N8 hydrogen bonds and each molecule B interlinks two neighboring molecules A into the other 1D infinite chain in the same way. Furthermore, the two dual chains are further stabilized by intermolecular C50-H50B···O1 hydrogen bonds to form an infinite 2D supramolecular network structure.

Key Words: Mono-oxime Compound, Crystal Structure, Supramolecular Interaction.

INTRODUCTION

Organic compounds containing imine groups are attracting increasing interest of the inorganic chemists nowadays. These kinds of compounds have been shown to be good ligands for transition metal ions and have found used widely[1,2]. The oxime-type compounds (-C=N-OR) are a kind of very important ligands which are easily prepared from the corres-ponding carbonyl compounds and hydroxylamine and are stable to hydrolysis compared with the corresponding imines[3-8]. The electrophilicity of the oxime carbon atoms is lower and addition of nucleophiles to O-substituted oximes does not proceed smoothly[9]. Because the oxime-type ligands are more stable to resist the metathesis of C=N bonds[10,11]. Therefore, to generate target relevent compounds by design, we choose ligands which can provide a way of controlling supramolecular intreactions. Meanwhile, ligands with symmetry are suitable for obtaining coordination supramolecules[12].

Phenyl-3-methyl-4-benzoyl-5-pyrazolinone (PMBP) is a β-diketone compound with potential to form different types of complex due to tautomeric effect of enol and keto form, a great number of reported oxime-type ligands has been synthesized by using PMBP *via* Schiff base reactions[13]. Herein, a new mono-oxime compound, (*Z*)-4-({4-[1-(hydroxyimino)-ethyl]phenylimino}(phenyl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one, has been synthesized and characterized.

EXPERIMENTAL

1-(4-Aminophenyl)ethanone (≥ 98.5 %) and hydroxyl-amine hydrochloride (≥ 98.5 %) were purchased from Shanghai Sanyou Reagent Factory and 4-benzoyl-3-methyl-1-phenyl-5-pyrazolinone (PMBP) (≥ 99.0 %) was purchased from chemical plant of East China Normal University and used without further purification. Other reagents and solvent were of analytical grade from Tianjin Chemical Reagent Factory. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. FT-IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr (4000-500 cm^{-1}) and Csl (500-100 cm^{-1}) pellets. X-ray single crystal structure was obtained on a Bruker Smart 1000 CCD area detector. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company.

General procedure: The title compound was synthesized according to a similar method reported earlier[14]. To an ethanol solution (4 mL) of 1-(4-aminophenyl)ethanone oxime (150.1 mg, 1 mmol) which was prepared using 1-(4-aminophenyl)-ethanone and hydroxylamine hydrochloride was added dropwise to a heated ethanol solution (6 mL) of PMBP (278.3 mg, 1 mmol). The mixture was stirred at 333-338 K for 15 h. The solvent was removed under reduced pressure and the residue was recrystallized from ethanol to give the yellow powder.

Yield, 73.8 %. m.p. 523-524 K. Several yellow block-like crystals suitble for X-ray diffraction studies were obtained by slow evaporation from a solution of dichloromethane at room temperature for about two weeks. Anal. calcd. (%) for $C_{25}H_{22}N_4O_2$: C, 73.14; H, 5.41; N, 13.66. Found (%): C, 73.29; H, 5.58; N, 13.12.

X-Ray structure determination: The single crystal of the title compound with approximate dimensions of 0.50 mm × 0.20 mm × 0.15 mm was placed on a Bruker Smart 1000 diffractmeter equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated MoK_α radiation (λ = 0.071073 nm) at 298(2) K. The LP factor and semi-empiriccal absorption corrections were applied to the intensity data. The structure was solved by using the program SHELXS-97 and difference Fourier techniques and refined by full-matrix least-squares method on F^2 using SHELXL-97. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. The data collection and refinements of the title compound was given in Table-1.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE TITLE COMPOUND

Empirical formula	$C_{25}H_{22}N_4O_2$
Formula weight	410.47
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Cell dimensions (Å)°	a = 9.5375(12), b = 11.2824(13), c = 20.545(2) α = 97.3970(10), β = 92.0430(10), γ = 99.280(2)
Volume (Å^3)	2160.1(4)
Z	4
Density (calculated) (mg/m^3)	1.262
Absorption coefficient (mm^{-1})	0.082
F(000)	864
Index ranges	$-1 \le h \le 11$, $-13 \le k \le 10$, $-24 \le l \le 22$
Reflections collected/unique	10989/7534 [R(int) = 0.0518]
Data/restraints/parameters	7534/0/559
Goodness of fit indicator	0.818
R [I > 2σ(I)]	R_1 = 0.0548, wR_2 = 0.0697
Largest diff. peak and hole	0.156 and -0.155 e.Å^{-3}

RESULTS AND DISCUSSION

FT-IR spectra: Key IR data of the title compound is given in Table-2. The IR spectrum exhibits several resonances in the 4000-500 cm^{-1} region. In the Table-2, it is clear that the title compound has obvious ν(O-H) absorption band at 3217 cm^{-1}, which indicates that the title compound exists with the imine enol type structure not the enamine ketonic. The absorption bands which appeared near the 2964, 2875 and 2292 cm^{-1} are assigned to ν(C-H) of the methyl or methylene. The absorption band of the title compound at 1732 cm^{-1} assigns to ν(C=O) to the pyrazole alkone ring. The ν(C-N) and ν(N-H) absorption bands of pyrazole ring are at 1384 cm^{-1} and 3059 cm^{-1}, respectively. The strong IR bands at 1616 and 1589 cm^{-1} are assigned to the ν(C=N) of the pyrazole ring and the alkyl chain.

Crystal structure description: X-ray crystallographic analysis reveals the crystal structure of the title compound. The bond lengths and bond angles are summarized in Tables 3 and 4. The ORTEP representation of the title compound is shown in Fig. 1. The title compound crystallizes in the triclinic system, space group P-1 and the unit cell contains two crystallographically independent but chemically identical molecules (molecules A and B, Fig. 1) consisting of a pyrazole ring, three benzene rings and a C=N-O group, *etc*. The dihedral angles between the central pyrazole (N1-N2-C1) and the benzene rings (C5-C10), (C12-C17) and (C18-C23) in molecules A are 31.73°, 66.29° and 48.77°, respectively. However, the dihedral angles between another central pyrazole (N5-N6-C26) and the related benzene rings (C30-C35), (C37-C42) and (C43-C48) molecules B are 37.02°, 71.93° and 60.75°, respectively. Consequently, the two molecular units are of distinct difference in structure.

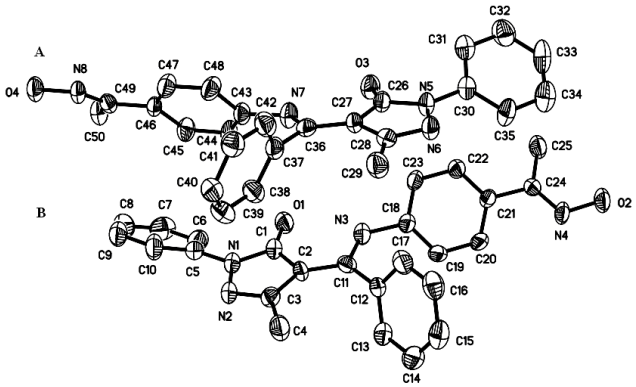

Fig. 1. Molecular structure of title compound with the atomic numbering. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level

Supramolecular interaction: In the crystal structure, there are two strong intramolecular N3-H3···O1 and N7-H7···O3 hydrogen bonds in molecules A and B between the -NH groups of the -C=NH groups and the ketone oxygen atoms of pyrazolone groups, which generate six-membered S(6) ring motifs (Table-5)[15-18]. In a pair of independent molecules A and B, each molecule A interlinks two neighbouring molecules B into a 1D infinite chain through six intermolecular O2-H2···N6, C29-H29A···O2, C35-H35···N4, O4-H4···N2, C4-H4A···O4 and C10-H10···N8 hydrogen bonds. And each molecule B interlinks two neighboring molecules A into the other 1D infinite chain in the same way (Fig. 2). In addition, two formed chains are held together by intermolecular C16-H16···O2, C23-H23···O3, C39-H39···O4 and C44-H44···O1 hydrogen bonds to form a 1D infinite dual chains (Fig. 3). Furthermore, this dual chains are further stabilized by intermolecular

TABLE-2
KEY INFRARED ABSORPTION BANDS (cm^{-1}) OF THE TITLE COMPOUND

Compound	ν(O-H)	ν(C-H)	ν(C=O)	ν(C-N)	ν(N-H)	ν(C=N)
$C_{25}H_{22}N_4O_2$	3217	2964, 2875, 2292	1732	1384	3059	1616, 1589

TABLE-3
SELECTED BOND LENGTHS (Å) OF THE TITLE COMPOUND

Bond	Length	Bond	Length	Bond	Length	Bond	Length
N(1)-C(1)	1.375(4)	O(3)-C(26)	1.247(4)	C(16)-C(17)	1.373(5)	C(33)-C(34)	1.373(6)
N(1)-N(2)	1.418(4)	C(1)-C(2)	1.439(5)	C(18)-C(19)	1.345(4)	C(34)-C(35)	1.391(5)
N(1)-C(5)	1.427(4)	C(2)-C(11)	1.412(4)	C(18)-C(23)	1.377(4)	C(36)-C(37)	1.482(5)
N(2)-C(3)	1.316(4)	C(2)-C(3)	1.433(4)	C(19)-C(20)	1.398(4)	C(37)-C(38)	1.382(5)
N(3)-C(11)	1.339(4)	C(3)-C(4)	1.503(4)	C(20)-C(21)	1.394(4)	C(37)-C(42)	1.383(5)
N(3)-C(18)	1.455(4)	C(5)-C(6)	1.382(5)	C(21)-C(22)	1.354(4)	C(38)-C(39)	1.372(5)
N(4)-C(24)	1.262(4)	C(5)-C(10)	1.384(5)	C(21)-C(24)	1.506(4)	C(39)-C(40)	1.374(5)
N(4)-O(2)	1.409(3)	C(6)-C(7)	1.404(5)	C(22)-C(23)	1.401(4)	C(40)-C(41)	1.371(5)
N(5)-C(26)	1.390(4)	C(7)-C(8)	1.362(5)	C(24)-C(25)	1.515(4)	C(41)-C(42)	1.380(5)
N(5)-N(6)	1.410(3)	C(8)-C(9)	1.376(6)	C(26)-C(27)	1.446(5)	C(43)-C(44)	1.357(4)
N(5)-C(30)	1.433(4)	C(9)-C(10)	1.403(5)	C(27)-C(36)	1.398(4)	C(43)-C(48)	1.396(5)
N(6)-C(28)	1.310(4)	C(11)-C(12)	1.471(5)	C(27)-C(28)	1.445(4)	C(44)-C(45)	1.389(4)
N(7)-C(36)	1.348(4)	C(12)-C(17)	1.383(5)	C(28)-C(29)	1.486(4)	C(45)-C(46)	1.382(4)
N(7)-C(43)	1.438(4)	C(12)-C(13)	1.387(5)	C(30)-C(35)	1.367(5)	C(46)-C(47)	1.392(4)
N(8)-C(49)	1.280(4)	C(13)-C(14)	1.381(5)	C(30)-C(31)	1.390(5)	C(46)-C(49)	1.474(4)
N(8)-O(4)	1.415(3)	C(14)-C(15)	1.371(5)	C(31)-C(32)	1.399(4)	C(47)-C(48)	1.372(4)
O(1)-C(1)	1.247(4)	C(15)-C(16)	1.392(5)	C(32)-C(33)	1.363(5)	C(49)-C(50)	1.500(4)

TABLE- 4
BOND ANGLES (°) OF THE TITLE COMPOUND

Bond	Angle	Bond	Angle	Bond	Angle
C(1)-N(1)-N(2)	112.4(3)	C(42)-C(37)-C(36)	120.8(5)	C(46)-C(45)-C(44)	121.6(4)
C(1)-N(1)-C(5)	127.2(4)	C(39)-C(38)-C(37)	119.7(5)	N(1)-C(1)-C(2)	104.1(4)
N(2)-N(1)-C(5)	120.3(3)	C(38)-C(39)-C(40)	121.4(5)	C(11)-C(2)-C(3)	131.1(4)
C(3)-N(2)-N(1)	105.8(3)	N(6)-N(5)-C(30)	119.3(3)	C(11)-C(2)-C(1)	122.3(4)
C(11)-N(3)-C(18)	127.6(3)	C(28)-N(6)-N(5)	105.8(3)	C(3)-C(2)-C(1)	106.5(3)
C(24)-N(4)-O(2)	112.5(3)	C(36)-N(7)-C(43)	125.5(3)	N(2)-C(3)-C(2)	111.1(4)
C(26)-N(5)-N(6)	113.7(3)	C(49)-N(8)-O(4)	111.9(3)	N(2)-C(3)-C(4)	118.6(4)
C(26)-N(5)-C(30)	127.0(4)	O(1)-C(1)-N(1)	125.4(4)	C(2)-C(3)-C(4)	130.2(4
C(6)-C(5)-C(10)	119.8(4)	O(1)-C(1)-C(2)	130.5(4)	C(21)-C(24)-C(25)	118.3(4)
C(6)-C(5)-N(1)	120.2(4)	C(14)-C(15)-C(16)	118.9(5)	O(3)-C(26)-N(5)	127.3(4)
C(10)-C(5)-N(1)	119.9(4)	C(17)-C(16)-C(15)	121.4(5)	O(3)-C(26)-C(27)	130.3(4)
C(5)-C(6)-C(7)	119.9(5)	C(16)-C(17)-C(12)	119.1(5)	N(5)-C(26)-C(27)	102.4(3)
C(8)-C(7)-C(6)	119.8(5)	C(19)-C(18)-C(23)	121.9(4)	C(36)-C(27)-C(28)	130.7(4)
C(7)-C(8)-C(9)	121.1(6)	C(19)-C(18)-N(3)	122.6(4)	C(36)-C(27)-C(26)	122.1(4)
C(8)-C(9)-C(10)	119.4(5)	C(23)-C(18)-N(3)	115.4(4)	C(28)-C(27)-C(26)	107.1(3)
C(5)-C(10)-C(9)	119.9(4)	C(18)-C(19)-C(20)	120.3(4)	N(6)-C(28)-C(27)	110.9(4)
N(3)-C(11)-C(2)	115.5(4)	C(21)-C(20)-C(19)	118.7(4)	N(6)-C(28)-C(29)	118.6(4)
N(3)-C(11)-C(12)	120.4(3)	C(22)-C(21)-C(20)	120.2(4)	N(6)-C(28)-C(29)	130.4(4)
C(2)-C(11)-C(12)	123.9(4)	C(22)-C(21)-C(24)	122.5(4)	C(35)-C(30)-C(31)	120.8(4)
C(17)-C(12)-C(13)	120.1(4)	C(20)-C(21)-C(24)	117.4(4)	C(35)-C(30)-N(5)	119.6(4)
C(17)-C(12)-C(11)	120.3(5)	C(21)-C(22)-C(23)	121.0(4)	C(31)-C(30)-N(5)	119.6(4)
C(13)-C(12)-C(11)	119.6(4)	C(18)-C(23)-C(22)	118.0(4)	C(30)-C(31)-C(32)	118.5(4)
C(14)-C(13)-C(12)	119.8(4)	N(4)-C(24)-C(21)	115.9(4)	C(33)-C(32)-C(31)	119.6(5)
C(15)-C(14)-C(13)	120.7(5)	N(4)-C(24)-C(25)	125.8(3)	C(45)-C(46)-C(47)	117.6(3)
C(32)-C(33)-C(34)	122.3(5)	C(41)-C(40)-C(39)	119.2(5)	C(45)-C(46)-C(49)	122.1(4)
C(33)-C(34)-C(35)	118.2(5)	C(40)-C(41)-C(42)	119.8(5)	C(47)-C(46)-C(49)	120.3(4)
C(30)-C(35)-C(34)	120.6(5)	C(41)-C(42)-C(37)	120.9(5)	C(48)-C(47)-C(46)	121.6(4)
N(7)-C(36)-C(27)	117.5(4)	C(44)-C(43)-C(48)	120.4(4)	C(47)-C(48)-C(43)	119.2(4)
N(7)-C(36)-C(37)	119.3(3)	C(44)-C(43)-N(7)	119.6(4)	N(8)-C(49)-C(46)	115.3(4)
C(27)-C(36)-C(37)	123.2(4)	C(48)-C(43)-N(7)	119.8(4)	N(8)-C(49)-C(50)	123.6(3)
C(38)-C(37)-C(42)	118.8(4)	C(43)-C(44)-C(45)	119.6(4)	C(46)-C(49)-C(50)	121.1(4)
C(38)-C(37)-C(36)	120.4(5)				

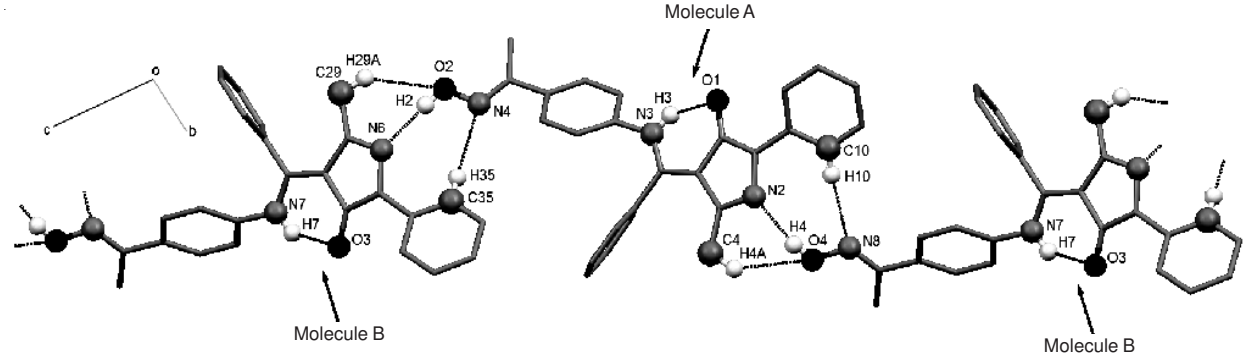

Fig. 2. Part of the infinite 1D chain motif of the title compound (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

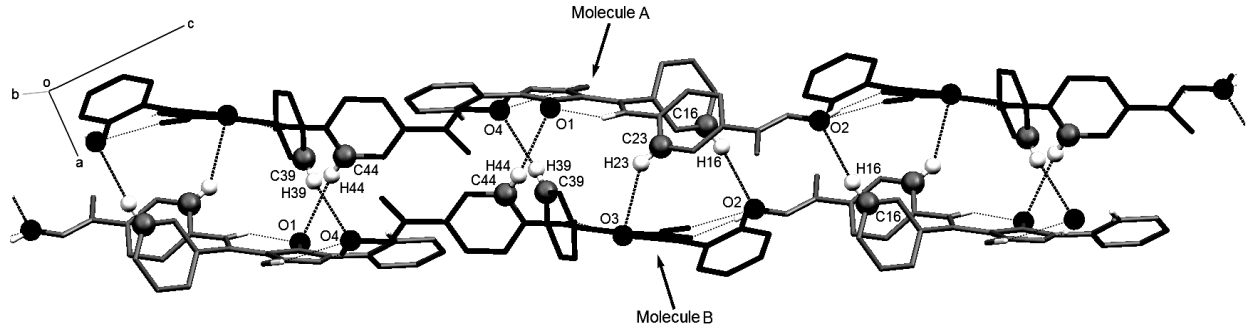

Fig. 3. Part of the infinite 1D chain motif of the title compound (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

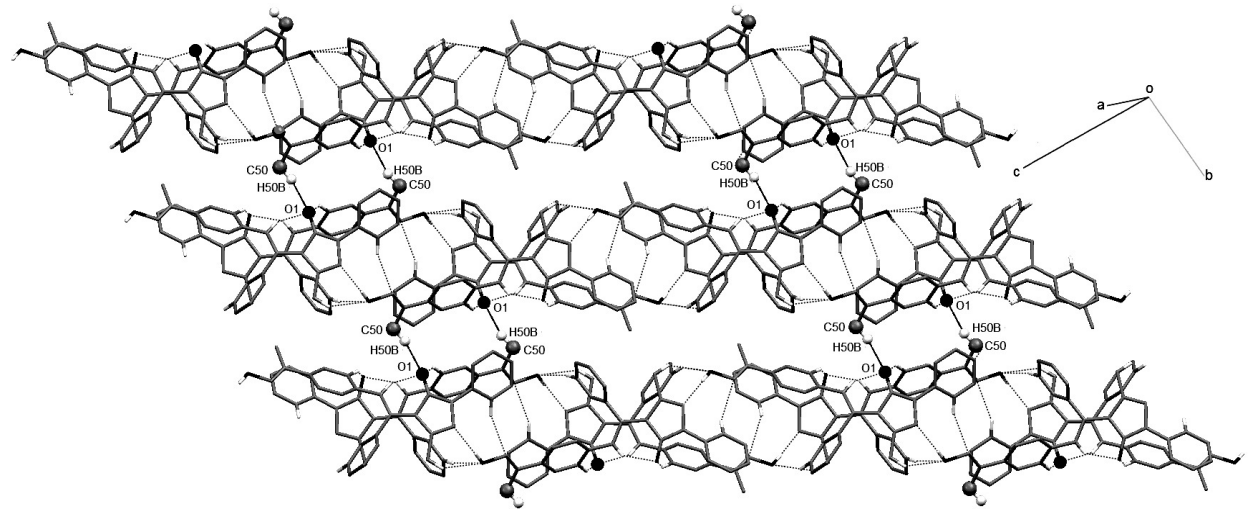

Fig. 4. View of infinite 2D supramolecular network of the title compound on the bc plane (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

TABLE-5
HYDROGEN BONDING DISTANCES (Å) AND BOND ANGLES (°) FOR THE TITLE COMPOUND

D-H...A	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠D-H···A
N3-H3···O1	0.86	1.95	2.674(3)	172
N7-H7···O3	0.86	2.01	2.705(3)	138
C44-H44···O1	0.96	2.26	2.639(3)	102
O2-H2···N6	0.82	2.04	2.851(3)	172
O4-H4···N2	0.82	2.05	2.804(3)	154
C4-H4A···O4	0.96	2.59	3.390(3)	140
C10-H10···N8	0.93	2.49	3.319(3)	149
C16-H16···O2	0.93	2.59	3.440(3)	152
C35-H35···N4	0.93	2.54	3.295(3)	139
C39-H39···O4	0.93	2.53	3.447(3)	169
C50-H50B···O1	0.96	2.38	3.217(3)	146

C50-H50B···O1 hydrogen bonds to form an infinite 2D supramolecular network (Fig. 4).

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