

Research Article

Hydrogen Bonded Supramolecular Motifs in the Crystal Structure of 2-[(2E)-2-(methoxyimino)-2-{2-[(2-methoxyphenoxy) methyl] phenyl} acetyl]-N-phenylhydrazinecarbothioamide

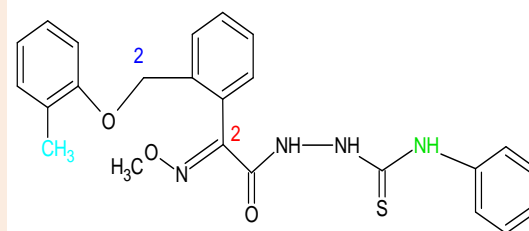
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Abstract

The title compound, C₂₄H₂₄N₄O₃S crystallizes in the monoclinic space group P2₁/n with unit cell parameters $a = 12.6304(10)$, $b = 7.5262(5)$, $c = 24.5372(17)\text{\AA}$, $\beta = 95.554(7)$, $Z = 4$. The supramolecular assembly in the title compound is built up by a network of strong N-H...O intermolecular interactions [viz N3-H3...O3 and N4-H4...O3] where oxygen atom (O3) act as a acceptor to both the hydrogen bonds forming motif R₂¹(6). Besides these interactions, the molecular structure is further consolidated by the existence of two intramolecular hydrogen bonding [N2-H2...S1 & N2-H2...N1] in which N2 acts as donar *via* H2 to both S1 and N1 in an almost planar three-centred system, forming 2S(5) motifs (Figure 2).



Keywords: X-ray Structure, Molecular Packing, Hydrogen Bonded Interactions, Graph Set Motif

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Introduction

Hydrogen bonding plays a key role in molecular recognition and crystal engineering. In the present work, we report the existence of bifurcated and three-centre hydrogen bonding. Such kind of unusual hydrogen bonds (HBs) are useful in explaining a large number of biological structures and are commonly used by biochemists and biologist to account for certain interactions in biological systems [1]. They can also be utilized for the design of the supramolecular architectures, as reviewed in related structures [2,3].

The title compound belongs to one of the many Strobilurins class of derivatives which are used as broad spectrum fungicides [4]. They possess a site-specific mode of action and exhibit higher efficiency than previously reported fungicides [5-8] against diseases affecting the economically important agricultural crops [9-11]. Such types of compounds can be easily metabolized in nature as well as in living systems and that is what makes their modifications of immense importance [9].

Experimental

Synthetic Procedure

(2E)-2-(methoxyimino)-2-{2-[(2-methylphenoxy)methyl]phenyl}ethanehydrazide (0.313mol) was refluxed with phenyl isothiocyanate (0.135 mol) in presence of absolute ethanol at about 8 hours to get white colored product. The synthesized compound [2-[(2E)-2-(methoxyimino)-2-{2-[(2-methoxyphenoxy) methyl] phenyl }acetyl]-N-phenylhydrazinecarbothioamide] is further dissolved in methanol and by the process of slow evaporation, white colored crystals were obtained.

X-Ray Intensity Data Collection

X-ray intensity data of the crystal (0.30 X 0.20 X 0.10 mm) having well-defined crystal morphology were collected at 293(2)K on X'calibur CCD area-detector diffractometer equipped with graphite monochromated MoK α radiation ($\lambda=0.71073\text{\AA}$). The intensities were measured by employing ω scan mode for the diffraction angle ranging from 3.64 to 26.00°. A total number of 8228 reflections were measured of which 4545 were found to be unique. The criterion ($I > 2\sigma(I)$) was employed to the unique data set and hence 2822 reflections were treated as observed. Data were corrected for Lorentz and Polarization factors. The structure was solved by direct methods using SHELXS97 [12]. All non-hydrogen atoms of the molecule were located in the best E-map and Full-matrix least-squares refinement was carried out using SHELXL97 [12]. All the hydrogen atoms were geometrically fixed and allowed to ride on the corresponding non-H atoms. The final refinement cycles converged to R = 0.0548 and wR(F²) = 0.1161 for 2822 observed reflections. Residual electron density ranges from -0.299 to 0.438 e \AA^{-3} . Atomic scattering factors were taken from International Tables for X-ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4).

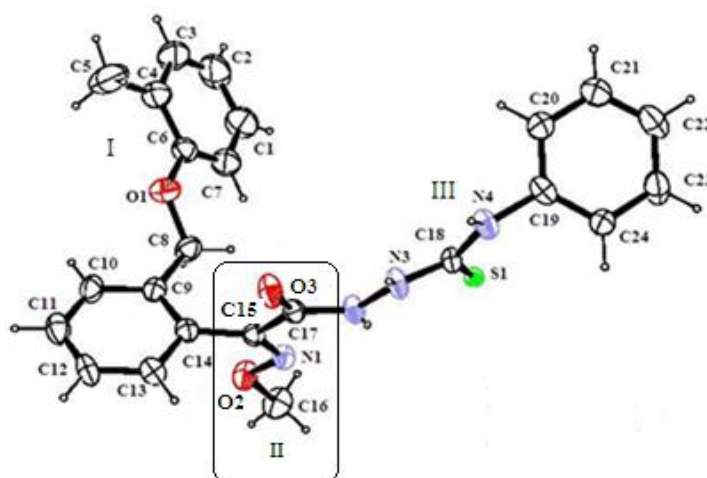
The crystallographic data are summarized in **Table 1**. Some selected bond angles which play an important role in collating the structural properties of this molecule with the related structures are presented in **Table 2**. An ORTEP [13] view of the molecule with atomic labeling is shown in **Figure 1**. The geometry of the molecule was calculated using the PLATON [14] and PARST [15] software. CCDC-1020777 contains the supplementary crystallographic data for this paper.

Table 1 Crystal data and other experimental details

System, sp. gr., Z	Monoclinic, P2 ₁ /n, 4
a, b, c Å	12.6304(10), 7.5262(5), 24.5372(17)
α, β, γ deg	90.000(0), 95.554(7), 90.000(0)
V, Å ³	2321.5(3)
D _x g.cm ⁻³	1.283
Radiation, λ , Å	MoK α , 0.71073
μ , mm ⁻¹	0.172mm ⁻¹
T, K	293
Sample size, mm	0.30X0.20X0.10
Diffractometer	Xcalibur, Sapphire3
Scan mode	ω
Absorption correction, T _{min} , T _{max}	Multi-scan, 0.61896, 1.00000
θ_{max} , deg	26.00
h, k, l ranges	h = -9 to 15, k = -8 to 9, l = -28 to 30
Number of reflections: measured/unique (N1), R _{int} /with $I > 2\sigma(I)$ (N2)	8228/4545
Refinement method	Full-matrix least-square on F ²
Number of refined parameters	291
R1/wR2 relative to N1	0.0548
R1/wR2 relative to N2	0.1161
S	1.062
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$, e/Å ³	0.438/-0.304
Programs	SHELXS97[12], SHELXL97[12]

Table 2 Selected bond lengths (Å) and bond angles (°) of the non-hydrogen atoms (e.s.d.'s are given in parentheses)

S1-C18	1.660(2)	N1-O2-C16	110.3(2)
O3-C17	1.236(2)	C18- N3- N2	118.9(2)
O2-N1	1.382(2)	O1-C8-C9	109.1(2)
O2-C16	1.433(3)	C4-C3-O1	115.0(3)
N3-C18	1.356(3)	C17- N2- N3	120.2(2)
N2-N3	1.377(2)	O3-C17-N2	122.8(2)
N2-C17	1.319(3)	N3-N2-C17	120.2(2)
N1-C15	1.280(3)	C15 -N1 -O2	111.4(2)
O1-C3	1.377(3)	O3 -C17 -C15	121.8(2)
O1-C8	1.417(3)	N4 -C18- N3	112.4(2)
C14-C9	1.398(3)	N4 -C18 -S1	126.0(2)
N4-C19	1.433(3)	N3 -C18- S1	121.6(2)
C13-C12	1.382(3)	N1- C15- C17	115.6(2)
C19-C20	1.368(4)	N2 -C17- C15	115.4(2)

**Figure 1** Ortep view of the molecules with displacement ellipsoids at the 40% probability level. H atoms are shown as small spheres of arbitrary radii. Here labels I, II, III indicates Methylphenoxy group, Methoxyimino group and Hydrazinecarbothiamide group respectively

Result and Discussion

The molecule comprises of three moieties, viz. Methylphenoxy (I), Methoxyimino (II) and Hydrazinecarbothiamide (III). The average distance for the bonds viz. C-O[1.382], S-C[1.660], N-N[1.377], N-C[1.357], N-H[0.86Å], is in agreement with the related structures [16, 17]. The phenyl rings confirm their ideal value (120°) for the endocyclic bond angles. The moiety I and II are essentially perpendicular to each other with dihedral angle 86.50°. The dihedral angle between moiety I and III 75.20° and between II and III is 70.72°. The methyl group in moiety II (attached to O2) takes up *anti-periplanar* (*trans*) orientation with torsion angle C16-O2-N1-C15= 174.2(2)° while S1 atom in the hydrazinecarbothiamide moiety is in *synperiplanar* conformation with respect to atom N2 and C19 [torsion angle being S1-C18-N4-C19= -4.4(4) and N2-N3-C18-S1=13.5(3)].

The supramolecular assembly is built up by a network of strong N-H...O intramolecular interactions [*viz* N4-H4...O3 and N3-H3...O3] where the oxygen atom (O3) acts as an acceptor to both the hydrogen bonds. Thus the bifurcated hydrogen bond leads to the formation of a graph set motif $R_2^1(6)$ [18]. There also exists three-centred intramolecular hydrogen bond [N2-H2...S1 & N2-H2...N1] in which N2 acts as a donor *via* H2 to both S1 and N1 in an almost planar three-centred system, forming $2S(5)$ motifs (**Figure 2**). The structure thus generated by these interactions gives rise to molecular sheets which are built through $R_2^2(10)$ and $R_2^2(14)$ rings moving them in a zig-zag fashion along the b-axis forming a supramolecular assembly (**Figure 3**). Hydrogen bond geometry details are presented in **Table 3**.

Table 3 Geometry of inter and intra-molecular hydrogen bonds

D-H...A	D-H(Å)	H...A(Å)	D...A(Å)	D-H...A (°)
N2-H2...S1	0.860	2.562	2.915	105.69
N2-H2...N1	0.860	2.263	2.625	105.31
N3-H3...O3 ⁱ	0.860	2.079	2.841	147.28
N4-H4...O3 ⁱ	0.860	2.146	2.934	152.08

Symmetry Codes: i) $-x+1, -y-1, -z$

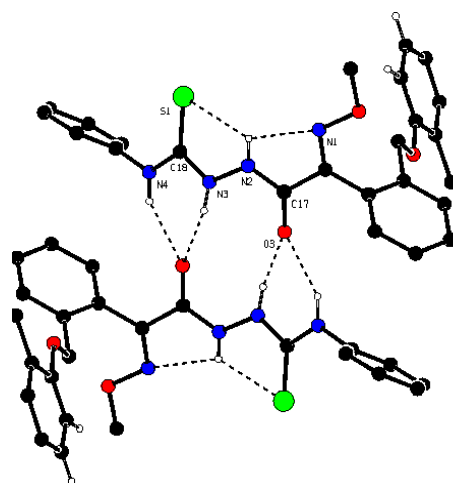


Figure 2 A plot of two molecules showing the formation of graph set motifs by inter and intra-molecular hydrogen bonds [N-H...O, N-H...S and N-H...N] shown by the dashed lines

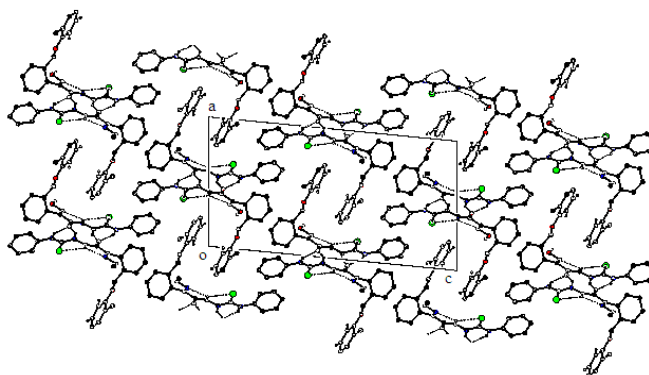


Figure 3 Packing of the molecules viewed down the b-axis

Conclusions

The compound 2-[(2E)-2-(methoxyimino)-2-{2-[(2-methoxyphenoxy)methyl]phenyl}acetyl]-N-phenyl-hydrazine carbothioamide has been synthesized by the reaction of (2E)-2-(methoxyimino)-2-{2-[(2-methylphenoxy)methyl]phenyl}ethanehydrazide with phenyl isothiocyanate in presence of absolute ethanol and characterized by single crystal X-ray diffraction with a final R-factor of 0.0548. The crystal structure is stabilized by the presence of a bifurcated and three-centred hydrogen bond. The structure as generated by these interactions results in the formation of continuous molecular sheets built from $R_2^2(10)$ and $R_2^2(14)$ rings along the *ac*-plane.

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