Research Article

Crystal Structure Analysis of (2*E*)-3-Methoxy-2-{2-[(2-methylphenoxy)methyl]phenyl}prop-2-enoic acid

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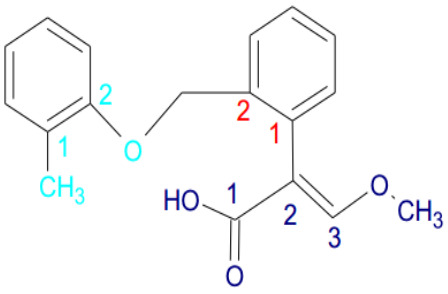
Abstract

(2*E*)-3-Methoxy-2-{2-[(2-methylphenoxy)methyl]phenyl} prop-2-enoic acid, $C_{18}H_{18}O_4$, crystallizes in the triclinic space group P-1 with unit cell parameters, a = 7.889(5)Å, b = 8.561(5)Å, c = 12.581(5) Å, α = 87.975(5)°, β = 82.295(5)°, γ = 65.684(5)° and number of molecules per unit cell (Z)=2. The structure was solved by direct methods using single-crystal X-ray diffraction technique and refined by full-matrix least-squares procedures to a final R-value of 0.0574 for 2263 observed reflections. In the crystal, pairs of O-H…O hydrogen bonds link molecules into inversion dimers featuring $R^2_2(8)$ graph set motif. Weak C-H…O hydrogen bond link these dimers into layers.

Keywords: X-ray Structure, Molecular Packing, Intermolecular Interactions, Direct Methods, Graph Set Motif



Chemical Structure

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Introduction

An important aspect in the rational design of bioactive molecules involves relating chemical structure to biological activity. Correlation of the results obtained from X-ray crystallography with biological activity has aided in the chemical design of few active agrochemicals. The strobilurins are an important and relatively new class of agricultural fungicides with a novel mode of action [1]. These have higher efficiency than previously reported fungicides [2-4] against various diseases [5,6] of economically important agricultural crops. Kresoxy-methyl is a widely used agricultural fungicide of the strobilurin group [7], with broad spectrum biological activity [8-10]. This type of compound is easily metabolized in nature as well as in living systems, and that is the reason studies on their fate in soil, plants and animal systems [6] are very important. In this paper, we report the structure of the title compound, which possesses fungicidal activity.

Experimental

Synthetic Procedure

Kresoxy-methyl (3.13 gm, 0.01mol) was refluxed with 2 gm of K_2CO_3 in presence of acetone 10ml and water 10 ml at about 15 hrs to get white coloured product. Newly synthesized compounds are further dissolved in alcohol and by the process of slow evaporation, yellowish coloured crystals were prepared.

X-Ray Intensity Data Collection

X-ray intensity data of a crystal (size: 0.30 X 0.20 X 0.20 mm) were collected at 293(2) K on an *X'calibur* CCD area-detector diffractometer equipped with graphite-monochromated Mo*Kα* radiation (λ=0.71073 Å). A total number of

5218 reflections were collected, of which 2996 were found to be unique. The intensities were measured by the ω scan mode for θ ranging over 4.05 to 26.00 °. A total number of 2263 reflections were treated as observed ($I > 2\sigma(I)$). Data were corrected for absorption and Lorentz-polarization factors. The structure was solved by direct methods using SHELXS97 [11]. All non-hydrogen atoms of the molecule were located from the best E-map. A full-matrix least-squares refinement was carried out using SHELXL97 [11]. All of the hydrogen atoms (except for the O4 H atom) were geometrically fixed, and allowed to ride on the corresponding non-H atoms with C-H= 0.93-0.97 Å and U_{iso} = 1.2 U_{eq}(C). The final refinement cycles converged to R = 0.0574 and wR (F^2) = 0.1545 for 2263 observed reflections. The residual electron densities ranged from -0.575to 0.454 eÅ^{-3}. The 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**. The selected bond lengths, bond angles and torsion angles are given in **Table 2**. An ORTEP view of the title compound with atomic labelling is shown in **Figure 1** [12]. The geometry of the molecule was calculated using PLATON [13] and PARST [14] software.

Results and Discussion

In the title compound, $C_{18}H_{18}O_4$, most of the bond distances and angles agree with the values observed for some related structures [15,16]. The phenyl rings are perfectly planar and the dihedral angle between them is 59.65°. The (methoxy)propenoic acid fragment is nearly perpendicular to the benzene ring [dihedral angle = 82.49°]. The four atom C6-O1-C7-C8 linkage between the phenyl rings assumes (-) *antiperiplanar* conformations [torsion angle = -173.53 (2)] °. The difference in bond distances between C6-O1 [1.374(3) Å] and C7-O1 [1.431 (2) Å] and correspondingly between C16-O2 [1.379(2) Å] and C17-O2 [1.433(4) Å] could be attributed to the different hybridization of Csp^2 and Csp^3 atoms. As such, the distance [1.218(3)Å] for C15=O3 corresponds to the existence of a double bond. Packing view of the molecules in the unit cell as viewed down the *a*-axis is shown in **Figure 2**. The O-H…O intermolecular hydrogen bond (O4-H1…O3) is responsible for the formation of a dimer (**Figure 3**) giving rise to the existence of $R^2_2(8)$ ring motif. There exists a single directed intermolecular bond (C11-H11…O4) which makes the dimers to form an infinite chain of molecules running diagonally to the *bc*-plane. The cumulative effect of these two intermolecular hydrogen interactions results in the formation of a supramolecular structure. The geometry of intermolecular interactions is given in **Table 3**.

Table 1 Crystal data and other experimental details

System, sp. gr., *Z*	triclinic, *P-1*, 2
a, *b*, *c* Å	7.889(5), 8.561(5), 12.581(5)
α, β, γ deg	87.975(5), 82.295(5), 65.684(5)
V, Å^3	767.1(7)
D_x g.cm^{-3}	1.184
Radiation, λ, Å	Mo*Kα*, 0.71073
μ, mm^{-1}	0. 091mm^{-1}
T, K	293
Sample size, mm	0.30X0.20X0.10
Diffractometer	Xcalibur, Sapphire3
Scan mode	*w*
Absorption correction, T_{min}, T_{max}	Multi-scan, 0.94516, 1.00000
θ_{max}, deg	26.00
h, *k*, *l* ranges	*h*= -6 to 9, *k* = -10 to 10, *l* = -14 to15
Number of reflections: measured/unique (*N*1), R_{int}/with $I > 2\sigma(I)$ (*N*2)	5218/2996
Refinement method	Full-matrix least-square on F^2

Number of refined parameters	206
R1/wR2 relative to *N*1	0.0574
*R*1/wR2 relative to *N*2	0.0766
S	1.050
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	0.454/-0.574

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

O1-C6	1.374(3)	C6-O1-C7	117.10(2)
O1-C7	1.431(3)	C16-O2-C17	109.3(2)
O2-C17	1.434(3)	O3-C15-O4	124.0(2)
O3-C15	1.218(3)	C6-O1-C7-C8	-173.53(2)
O4-C15	1.293(3)	C13-C14-C15-O3	8.0(3)
C16-O2	1.379(3)	O2-C16-C14-C13	2.3(3)
C16-C14	1.267(3)	O2-C16-C14-C15	117.28(2)

Table 3 Geometry of intermolecular hydrogen bonds

D-H….A	D-H(Å)	H…A(Å)	D…A(Å)	D-H….A (º)
O4-H1…O3^{i}	1.03(4)	1.61(4)	2.634(3)	171(4)
C11-H11…O4^{ii}	0.93	2.60	3.40(4)	145

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

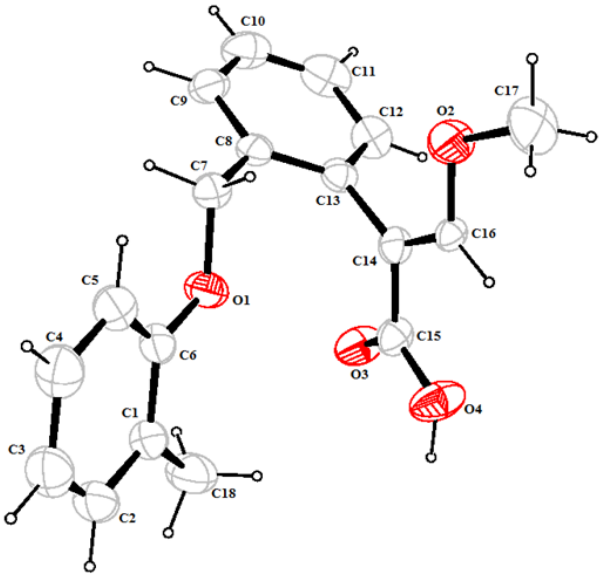

Figure 1 ORTEP view of the molecules with displacement ellipsoids at the 40% probability level

H atoms shown as small spheres of arbitary radii

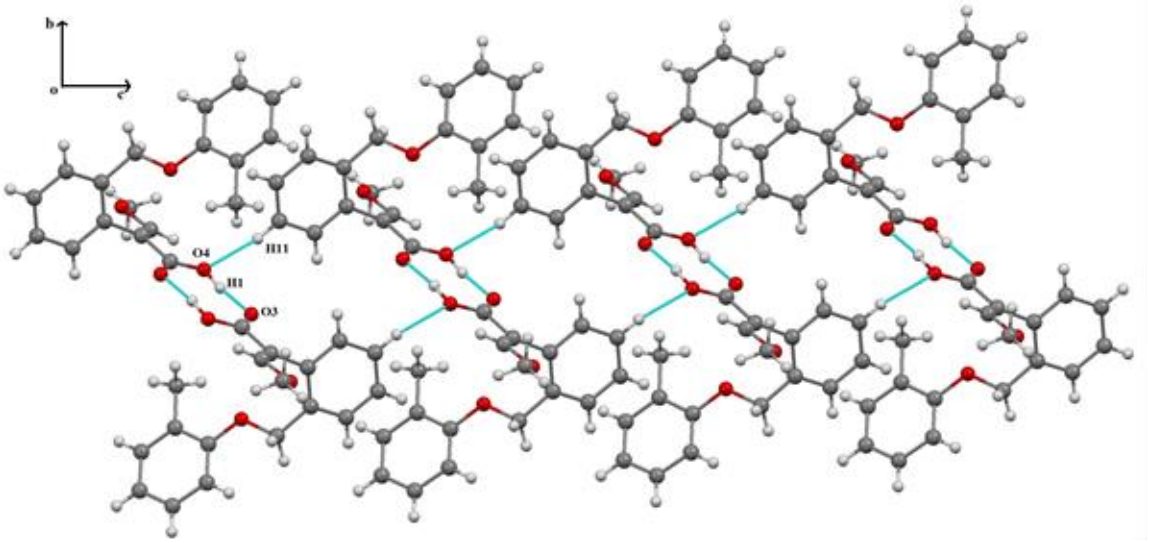

Figure 2 Packing of the molecules viewed down the a-axis

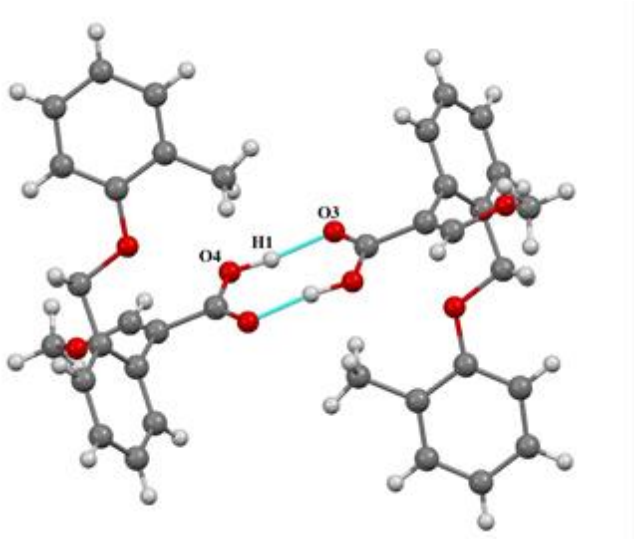

Figure 3 A dimer formed by intermolecular O-H….O hydrogen bonds

Conclusions

The compound (2*E*)-3-Methoxy-2-{2-[(2-methylphenoxy)methyl]phenyl}prop-2-enoic acid has been synthesized from kresoxy-methyl in the presence of acetone and then prepared by slow evaporation method under ambient conditions. The structure was characterized by single crystal X-ray diffraction with a final R-factor of 0.0574. In the crystal packing O4-H1…O3 intermolecular hydrogen bonds link the molecules into dimers forming $R^2_2(8)$ ring motifs. The crystal structure is further stabilized by C11-H11…O4 intermolecular hydrogen bond that results a supramolecular structure along *bc-plane*.

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