

Synthesis and Structural Analysis of the Crystal Methyl 3,5-BIS(Ethynyloxy)Benzoate

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Abstract; In the title compound, C₁₄ H₁₃ O₄, the benzene ring is surrounded by two Oxygen atoms and a Carbon atom. In the crystal, molecules are linked by C—H... π interactions. The chains are linked by offset π – π interactions [intercentroid distance = 3.9702(11) Å], forming sheets lying parallel to (011).

INTRODUCTION;

Esters are a class of organic compounds which are of synthetic interest. Esters of salicylic acid such as acetyl salicylic acid (phenolic ester), phenyl salicylate and methyl salicylate (carboxylic esters) are widely used as drugs (Khanum et al., 2005). The vast significance of such esters has enhanced the interest in exploring their structure–activity relationships and to search for esters as biological lead compounds. In order to obtain more detailed information about the effect of substitution of the methyl groups on the structure of benzoate system, the structure determination of methyl 3,5- bis(ethynyloxy)benzoate has been carried out.

Benzoate derivatives have drawn much attention because of their medicinal activities, such as anti-microbial (Ankersen et al., 1997) and anticancer (Reveszet al., 2004). There are many methods documented for the synthesis of a wide range of aromatic carboxylic acid derivatives. These compounds can be prepared using palladium(0)-catalyzed carbonylation of aryl halides with various nucleophiles (Zhao *et al.*, 2008; Margerleinet *al.*, 2001; Stille & Wong, 1975).

MATERIALS AND METHODS

MATERIALS

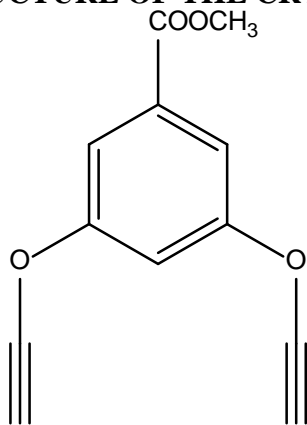
3,5-dihydroxy benzoic acid (10 ml), magnesium hydroxide, bromine water, K₂CO₃

METHOD(EXPERIMENTAL)

On slowly heating of 3,5-dihydroxy benzoic acid (10 ml) for eighteen hours with magnesium hydroxide in presence of con. H₂SO₄ a pleasant smelling liquid-methyl 3,5- dihydroxy benzoate

is formed. After the reduction reaction is over, the compound is again goes to esterification with bromine water in presence of K_2CO_3 , it gives methyl 3,5-bis(ethynyloxy)benzoate. This reaction has time for forty eight hours. Light yellow odour crystals were obtained after one week.

STRUCTURE OF THE CRYSTAL:



methyl 3,5-bis(ethynyloxy)benzoate

DATA COLLECTION

Bruker SMART APEXII CCD diffractometer, Radiation source: fine-focus sealed tube, Graphite monochromator ω and ϕ scans, Absorption correction: multi-scan (*SADABS*; Bruker, 2008), $T_{min} = 0.964$, $T_{max} = 0.979$

COMPUTER PROGRAMS

APEX2, SAINT and XPREP (Bruker, 2004), SHELXS97 and SHELXL97 (Sheldrick, 2008), ORTEP-3 for Windows (Farrugia, 1997) and PLATON (Spek, 2009).

RESULTS

ORTEP

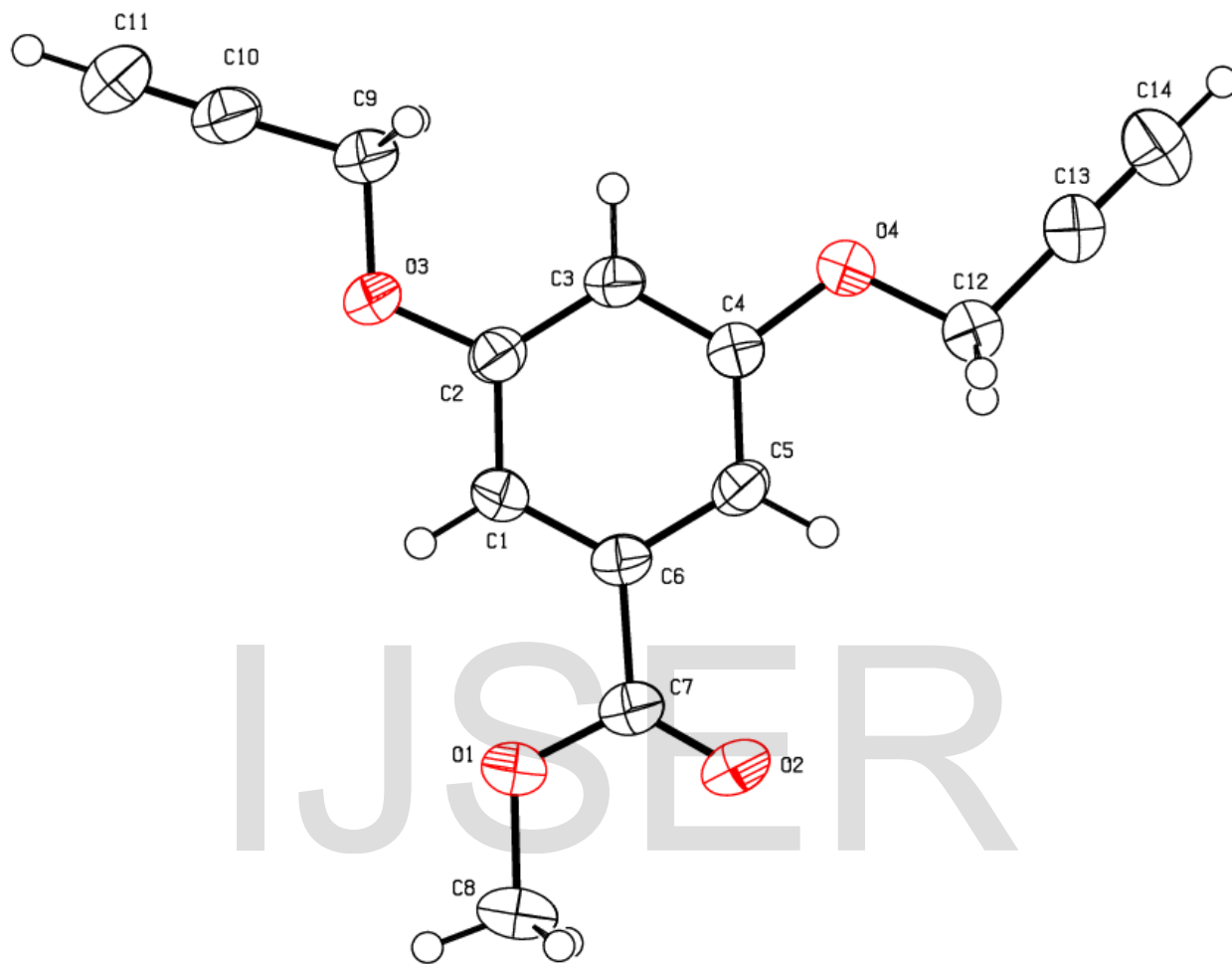
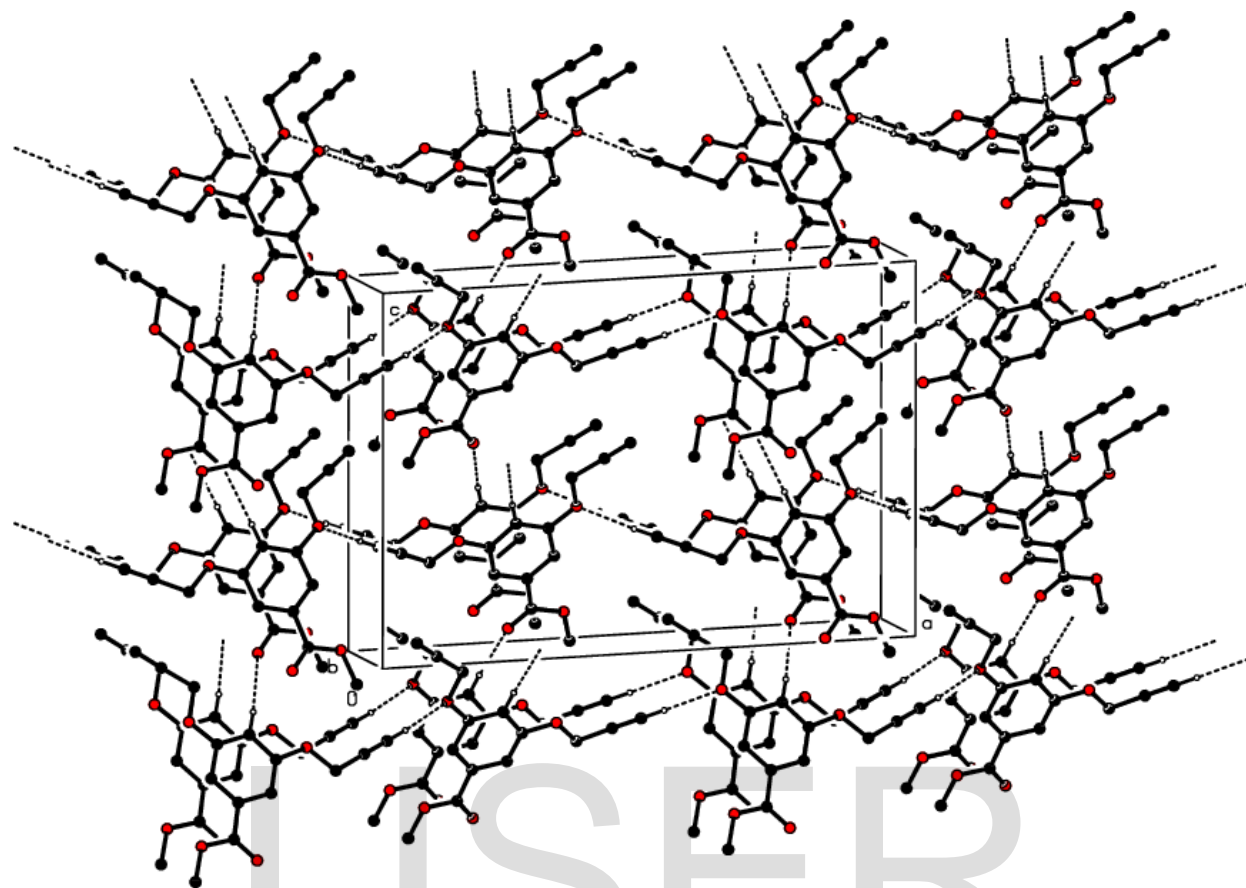


Figure 1(ORTEP)

The molecular structure of the title compound, with the atomic numbering scheme and displacement ellipsoids drawn at 30% probability level.

PACKING (1)



A partial view of the crystal packing of the title compound is viewed along (011) showing intramolecular hydrogen bonds in sheet like structure.

Table 1:

Hydrogen-bonding geometry (\AA , $^\circ$) D-Donor, H-Hydrogen, A-Acceptor

D-H-A	D-H	H-A	D-A
C3-H3-O2	0.93	2.51	3.436
C14-H14-O3	0.93	2.35	3.276

Table 2:

Selected geometric parameters, Torsion angles(\AA , $^\circ$)

C5-C6-C7-O1	177.07 (17) $^\circ$
C6-C7-O1-C8	179.55 (17) $^\circ$
C7-C6-C1-C2	178.90 (16) $^\circ$
C6-C1-C2-O3	179.83 (17) $^\circ$

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Table 3;

Experimental details

Crystal data Chemical formula	C ₁₄ H ₁₃ O ₄
M _r	245.24
Crystal system, space group	Orthorhombic, Pca21
Temperature(K)	293(2)
a, b, c, (Å)	21.4656(17), 3.9702(3), 14.4908(12)
β(°)	90
V(Å ³)	1234.95(17)
Z	4
Radiation type	Mo Kα
μ(mm ⁻¹)	0.11
Crystal size (mm)	0.65 X 0.45 X 0.25
Data collection Diffractometer	Bruker SMART APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2008)
Tmin, Tmax	2.31, 25.000
No. of measured, independent and observed [I > 2σ(I)] reflections	1134
R _{int}	0.0420
(sin Θ/λ) _{max} (A° ⁻¹)	0.0472
Refinement R[F ² > 2σ(F ²)], wR(F ²), S	0.0339, 0.0832, 0.989
No. of reflections	13567
No. of parameters	163
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	17, -17

DISCUSSION

Comment;

The crystal packing shows no classical hydrogen bonds and it is stabilized by weak C—H · · O Intermolecular hydrogen bonds, forming $C(6)$ chains (Etter, 1990) along [011]. The C3 atom acts as hydrogen-bond donor to O2 atom at $(x-1, +y, +z)$ (Nardelli, 1995). The aromatic rings are close to planar [C5—C6—C7—O1, 177.07 (17)°; C6—C7—O1—C8, 179.55 (17)°], The aromatic chain has an extended conformation, as indicated by the C7—C6—C1—C2 torsion angle of 178.90 (16)°, and lies in the same plane of the C6—C1—C2—O3 benzene ring, subtending torsion angle of 179.83 (17)°.

The main skeleton of the crystal is formed by the Benzene ring is illustrated in ortep figure. The aromatic ring (C1—C2—C3—C4—C5—C6) and the ester O2—C7—O1—C8 are close to planar. In the crystal, molecules are linked by C-H... π interactions, forming chains propagating along the b and c-axis direction and give the packing diagram as the sheet like structure. The chains are linked by offset π — π interactions [intercentroid distance = 3.9702(11) Å], forming sheets with symmetry code X, 1+Y, Z.

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