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ORIGINAL PAPER

Crystal Structure of [4-(Methylsulfanyl)Phenyl]Acetic Acid

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Abstract The title compound, $C_9H_{10}O_2S$, (I), crystallizes in the triclinic space group, $P-1$, with unit cell parameters $a = 6.2249(3)$, $b = 7.3733(5)$, $c = 19.5708(12)$, Å, $\alpha = 86.746(5)°$, $\beta = 88.682(5)°$, $\gamma = 86.988(5)°$, $Z = 4$. The molecule consists of a methyl sulfanyl group bonded to benzyl acetic acid at the 4 position crystallizing with two molecules in the asymmetric unit. The carboxylic acid group from the acetic acid moiety in these two molecules forms a classic O–H···O hydrogen bonded dimer with O···O distances of 2.673(2) and 2.646(2) Å, in a R_2^2 (8) graph-set motif which link the molecules into pairs around inversion centers in the unit cell. The dihedral angles between the mean planes of the R_2^2 (8) graph-set motif with the mean planes of the two nearby benzyl groups within the same dimer in the unit cell are 64.1(6)° and 71.3(4)°, respectively. Within the same dimer the dihedral angle between the two benzyl groups is 45.2(1)°. The structure is supported by a weak intermolecular C–H···Cg π-ring interaction and gives support to molecular packing stability in the unit cell. Comparison to a MOPAC AM1 computational calculation provides support to these observations.

Keywords Acetic acid · Methyl sulfanyl · Carboxylic acid · Dimer · R_2^2 (8) graph-set motif · MOPAC

Introduction

Phenylacetic acids serve as an ingredient in perfume to provide honey-like odor. It is found as a moiety in some alkaloids and plant hormone and is formed as catabolite of phenylalanine. In the toluic acid nomenclature system, phenylacetic acid is an alpha-toluic acid in which one of the hydrogen atoms in the methyl group has been substituted for instead of a substitution in the benzene ring. Substituted phenylacetic acid molecules at the alpha position and phenylacetate esters can serve as a drug with a wide variety of effects including anticholinergic, muscarinic antagonist as well as an antidote to cholinesterase inhibitors or toxins. Cycloplegic and mydriatic phenylacetic acid is used to prepare a nonsteroidal anti-inflammatory drug like diclofenac [1, 2]. It is used the manufacture of penicillin. Mandelic acid and phenylglycollic acid can be produced from phenylchloracetic acid. A related compound, indole-3-acetic acid, which promotes cell elongation in plants, has been isolated from plants and has served as a stimulus to search for similar compounds of related structure thereby creating renewed interest in substituted phenylacetic acids. Structures of few related acids are known via: phenlyacetic acid [3], (2-ethoxy-5-indanyl)acetic acid [4], 2-methoxy-2-phenylacetic acid [5],

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p-nitrophenylacetic acid [6], indoprofen: 2-[4-(1-oxo-2-isoindolinyl)phenyl]propionic acid [7], [4-(phenoxymethyl)phenyl]acetic acid [8], [4-(benzyloxy)phenyl]acetic acid [9] and 3-(2-furyl)-2-phenylpropenoic acid [10]. A new derivative, [4-(methylsulfanyl)phenyl]acetic acid, (I), is synthesized and its crystal structure is reported here.

Experimental

[4-(Methylsulfanyl)phenyl]acetonitrile (4.89 g, 0.03 mol) was refluxed for 1 h with dilute sulfuric acid (15 mL conc. sulphuric acid diluted with 14 mL water). The reaction mixture was diluted with 30 mL water and cooled to 273 K. The separated solid was filtered and recrystallized from acetone. mp: 370–371 K. Composition for $C_9H_{10}O_2S$: Found (Calculated): C: 59.27 (59.32); H: 5.49 (5.53); S: 17.53% (17.59%).

Structure Determination and Refinement

X-ray data for (I) was collected with an Oxford Diffraction Gemini R CCD area detector using *CrysAlisPro* software and graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) at

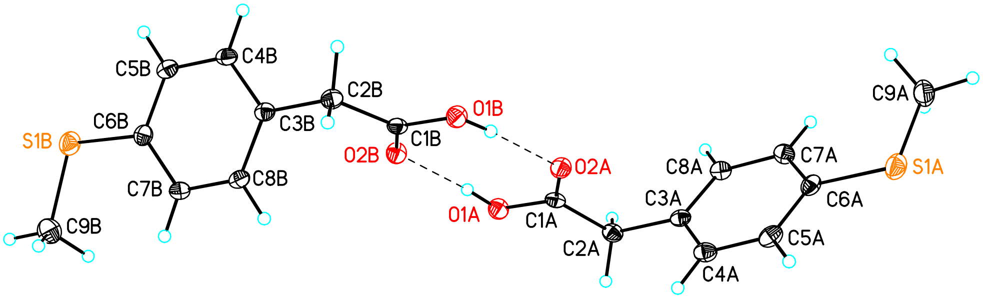


Fig. 1 ORTEP drawing of (I) showing the atom numbering scheme of the asymmetric unit containing two molecules and 50% probability displacement ellipsoids of non-H atoms. *Dashed lines* indicate intermolecular hydrogen bonds between carboxyl acceptor atoms O(1) and O(2) (O(1)···H(2B)–O(2)) which form an R_2^2 (8) graph-set motif arrangement

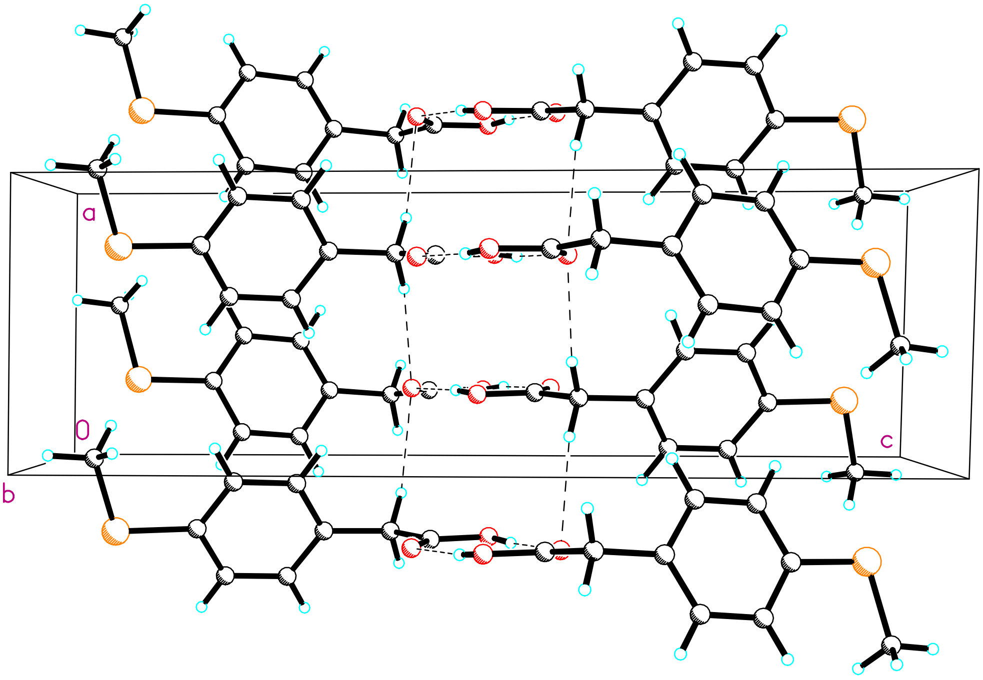
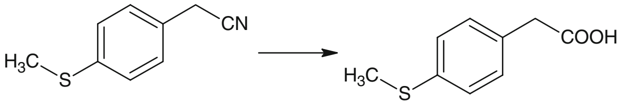


Fig. 2 The molecular packing for (I) viewed down the *b* axis. *Dashed lines* indicate both intermolecular hydrogen bonds between carboxyl acceptor atoms O(1A)···O(2B) and O(1B)···O(2A) (O(2B)···H(1A)–O(1A) and (O(2A)···H(1B)–O(1B)) forming a dimer and weak intermolecular C–H···O interactions (C(2A)–H(2AA)···O(2B)#1; C(2A)–H(2AB)···O(2B)#2; C(2B)–H(2BA)···O(2A); C(2B)–H(2BB)···O(2A)#3 where #1 = −1 + *x*, −1 + *y*, *z*; #2 = *x*, −1 + *y*, *z*; #3 = 1 + *x*, *y*, *z*) which provide support for the classic O–H···O hydrogen bonded dimer molecules to become arranged into chains along the (101) plane of the unit cell

200(2) K. The structure was solved by direct methods using SHELXS97 [11] and all of the non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using SHELXL97 [11]. The hydrogen atoms were placed in their calculated positions and included in the refinement using the riding model. An absorption correction was performed using *CrysAlis RED* and all calculations, including Figs. 1 and 2, were performed using SHELXTL [12]. Crystal and experimental data for (I) are listed in Table 1. Scheme 1 for the molecular structure of (I) is shown. Bond lengths and bond angles are all within expected ranges, Table 2 [13].

Table 1 Crystal and experimental data for (I)

Formula	$C_9H_{10}O_2S$
Formula weight	182.23
Crystal color, habit	Colorless, chunk
Crystal size (mm)	0.53 × 0.46 × 0.32
Crystal system	Triclinic
Space group, *Z*	*P* − 1, 4
Temperature (K)	200(2)
a (Å)	6.2249(3)
b (Å)	7.3733(5)
c (Å)	19.5708(12)
α (°)	86.746(5)
β (°)	88.682(5)
γ (°)	86.988(5)
Volume (Å^3)	906.39(9)
F(000)	384
Absorption coef (mm^{-1})	0.316
D_{calc} (Mg m^{-3})	1.352
No. of reflections [$I > 2\sigma(I)$]	7124
$2\theta_{max}$ (°) with Mo K_a	69.6
R, R_w [$I > 2\sigma(I)$]	0.0737, 0.1760
$(\Delta\rho)_{max/min}$ (e Å^{-3})	0.602/−0.315
GOF on F^2	1.037
Measurement	*GEMINI* (Oxford Diffraction 2007)
Program system	*CrysAlisPro*
Structure determination	*SHELXS97*
Refinement	Full-matrix least-squares on F^2 (*SHELXL97*)



Scheme 1 Chemical synthesis of the title compound, $C_9H_{10}O_2S$, (I)

Results and Discussion

The title compound, $C_9H_{10}O_2S$, consists of a methyl sulfanyl group bonded to benzyl acetic acid at the 4 position crystallizing with two molecules in the asymmetric unit. The carboxylic acid group from the acetic acid moiety in these two molecules forms a classic O–H···O hydrogen bonded dimer with O(1A)···O(2B) and O(1B)···O(2A) distances of 2.673(2) and 2.646(2) Å, respectively, (Table 3) in a R_2^2 (8) graph-set motif [14] which link the molecules into pairs around inversion centers in the unit cell (Fig. 1). The O–H···O hydrogen-bonded interactions involving these pairs are very strong and stabilize molecular packing of these dimers into a unique assembly. The torsion angles of the two carboxylic acid groups that form the dimer indicate that the plane of the R_2^2 (8) graph-set motif deviates slightly from planarity (O1A–C1A–C2A–C3A, 174.62(16); O2A–C1A–C2A–C3A,-6.1(3); O1B–C1B–C2B–C3B, -177.41 (16); O2B–C1B–C2B–C3B, 2.3(3)). This is supported by the calculation of the dihedral angle between the mean planes of the carboxyl groups forming the dimer which is 9.7(3)°. The dihedral angles between the mean planes of the R_2^2 (8) graph-set motif with the mean planes of the two nearby benzyl groups within the same dimer in the unit cell are 64.1(6)° and 71.3(4)°, respectively. Within the same dimer the dihedral angle between the two benzyl groups is 45.2(1)°. The distance between the centroids of adjacent nearly parallel R_2^2 (8) graph-set motif 's is 4.99(2) Å with a slippage angle of 49.6(7)° providing a small effect on molecular packing from these groups in the unit cell.

The structure is supported by a weak intermolecular C–H···Cg2 π-ring interaction at x, $-1 + y$, z, where Cg2 = center of gravity of a benzene ring (C(3B)–C(8B), C(8A)···Cg2 = 3.630(9) Å, C(8A)–H(18AA)···Cg2 = 126.(1)°), and gives support to molecular packing stability in the unit cell.

A MOPAC AM1 calculation was performed on the $C_9H_{10}O_2S$ dimer with *WebMO Pro* [15] (AM1 (Austin Model 1) approximation together with the Hartree-Fock closed-shell (restricted) wavefunction was used and minimizations were teminnated at an r.m.s. gradient of less than 0.01 kJ mol^{-1} Å^{-1}). Starting geometries were taken from X-ray refinement data. As a result the only bond lengths that changed significantly were those for C(6A)–S(1A) (1.761(2) vs.(1.692) Å) and C(6B)–S(1B) (1.759(2) vs. (1.692) Å) which were shortened somewhat. However, a number of angles and torsion angles show significant differences when compared to the values from the crystal structure which are listed in Table 2. The angles and torsion angles associated with the carboxyl group from each molecule that form the dimer through the R_2^2 (8) graph-set motif have changed significantly causing an out-of-plane twist away from planarity. The dihedral angle between the

Table 2 Selected geometric parameters for (I) (Å, °)

C(1A)–O(1A)	1.317(2)	(1.358)[a]	C(1A)–O(2A)	1.219(2)	(1.238)[a]
C(1B)–O(1B)	1.322(2)	(1.357)[a]	C(1B)–O(2B)	1.216(2)	(1.237)[a]
C(1A)–C(2A)	1.504(3)	(1.498)[a]	C(1B)–C(2B)	1.500(3)	(1.501)[a]
C(6A)–S(1A)	1.761(2)	(1.692)[a]	C(6B)–S(1B)	1.759(2)	(1.692)[a]
O(1A)–C(1A)–O(2A)	123.15(18)	(117.01)[a]	O(1B)–C(1B)–O(2B)	122.98(18)	(117.29)[a]
O(1A)–C(1A)–C(2A)	113.22(16)	(113.20)[a]	O(1B)–C(1B)–C(2B)	112.71(16)	(113.46)[a]
O(2A)–C(1A)–C(2A)	123.62(18)	(129.76)[a]	O(2B)–C(1B)–C(2B)	124.31(18)	(129.22)[a]
C(6A)–S(1A)–C(9A)	103.95(12)	(106.08)[a]	C(6B)–S(1B)–C(9B)	103.98(12)	(105.95)[a]
O(1A)–C(1A)–C(2A)–C(3A)	174.62(16)	(142.21)[a]	O(1B)–C(1B)–C(2B)–C(3B)	−100.6(3)	(136.67)[a]
O(2A)–C(1A)–C(2A)–C(3A)	−6.1(3)	(−39.94)[a]	O(2B)–C(1B)–C(2B)–C(3B)	145.55(18)	(−45.47)[a]
C(5A)–C(6A)–S(1A)–C(9A)	−172.71(16)	(178.73)[a]	C(5B)–C(6B)–S(1B)–C(9)	−173.23(18)	(0.63)[a]

[a] MOPAC computation results (Å, °) [15]

Table 3 Hydrogen bonds for (I) (Å and °)

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O(1A)–H(1A)···O(2B)	0.84	1.84	2.673(2)	174.8
O(1B)–H(1B)···O(2A)	0.84	1.81	2.646(2)	175.4
C(2A)–H(2AA)···O(2B)#1	0.99	2.47	3.461(1)	175.1
C(2A)–H(2AB)···O(2B)#2	0.99	2.54	3.406(4)	146.1
C(2B)–H(2BA)···O(2A)	0.99	2.50	3.475(5)	167.1
C(2B)–H(2BB)···O(2A)#3	0.99	2.49	3.454(7)	164.1

Symmetry transformations used to generate equivalent atoms: #1 $-1 + x, -1 + y, z$; #2 $x, -1 + y, z$; #3 $1 + x, y, z$

mean planes of the carboxyl groups forming the dimer increases from 9.7(3)° in the crystal to 27.6(6)° in the computation. The dihedral angles between the mean planes of the R^2_2 (8) graph-set motif with the mean planes of the two nearby benzyl groups within the same dimer in the unit cell change from 64.1(6)° and 71.3(4)° to 30.7(8)° and 41.0(6)°, respectively. And within the same dimer, the dihedral angle between the two benzyl groups changes from 45.2(1)° to 71.7(8)°. It is clear that changes in the bond distances involving the sulphur atom (S(1A) and S(1B)) and distortions of the bond angles and torsion angles of the atoms that comprise the carboxyl group forming the dimer are significantly influenced by the strength of the strong O–H···O intermolecular interactions as well as the weak intermolecular C–H···O hydrogen bonding and π-ring interactions that are observed.

Supporting Information Available

X-ray crystallographic files, in Cif format, for the structure determinations of (I) (711542) has been deposited with the Cambridge Crystallographic Date Center, CCDC: 26091. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or at: http://www.ccdc.cam.ac.uk).

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