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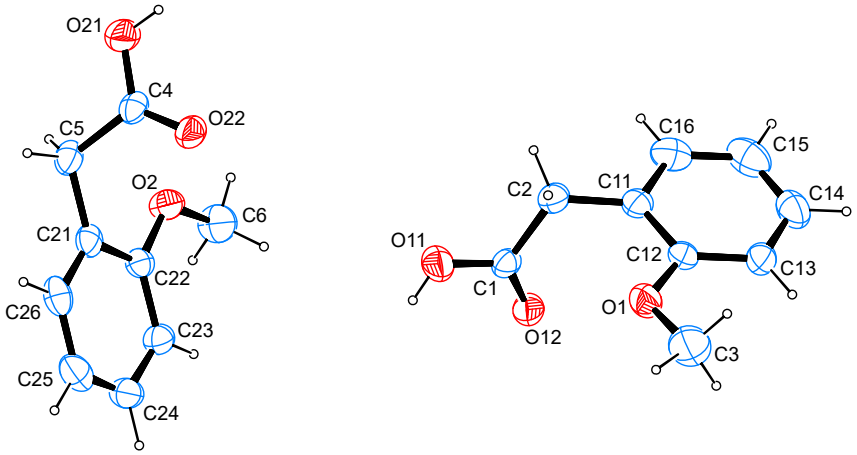
The crystal structure of 2-(2-methoxyphenyl) acetic acid, $C_9H_{10}O_3$



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Abstract

$C_9H_{10}O_3$, orthorhombic, *Pbca* (no. 61), a = 14.2570(6) Å, b = 7.9250(4) Å, c = 29.8796(13) Å, V = 3376.0(3) Å^3, Z = 16, $R_{gt}(F)$ = 0.0404, $wR_{ref}(F^2)$ = 0.1050, T = 200 K.

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The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The compound was obtained commercially (Riedel de Haen). Crystals suitable for the diffraction study were taken directly from the provided product.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.31 × 0.23 × 0.20 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.10 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	30,439, 4241, 0.033
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 $\sigma(I_{obs})$, 3000
$N(param)_{refined}$:	221
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å for aromatic carbon atoms, C–H 0.99 Å for methylene groups) and were included in the refinement in the riding model approximation, with U(H) set to 1.2U_{eq}(C).

The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C–C bond to best fit the experimental electron density (HFIX 137 in the *SHELX* program suite [3]), with U(H) set to 1.5U_{eq}(C).

The H atoms of the hydroxyl groups were allowed to rotate with a fixed angle around the C–O bond to best fit the experimental electron density (HFIX 147 in the *SHELX* program suite [3]), with U(H) set to 1.5U_{eq}(O).

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1	0.63057 (7)	0.46864 (13)	0.06617 (3)	0.0409 (3)
O11	0.42514 (7)	0.19190 (14)	0.11188 (3)	0.0426 (3)
H11	0.435893	0.125708	0.133234	0.064*
O12	0.55778 (6)	0.08032 (12)	0.08559 (3)	0.0358 (2)
C1	0.49170 (9)	0.17780 (17)	0.08196 (4)	0.0292 (3)
C2	0.47619 (9)	0.28975 (19)	0.04214 (4)	0.0367 (3)
H2A	0.458757	0.403611	0.052942	0.044*
H2B	0.422414	0.245191	0.024832	0.044*
C3	0.69844 (13)	0.5903 (2)	0.07896 (5)	0.0601 (5)
H3A	0.759999	0.536042	0.081433	0.090*
H3B	0.681022	0.639064	0.107927	0.090*
H3C	0.701193	0.679729	0.056355	0.090*
C11	0.55892 (9)	0.30634 (17)	0.01122 (4)	0.0313 (3)
C12	0.63624 (9)	0.40156 (16)	0.02421 (4)	0.0298 (3)
C13	0.71167 (10)	0.42547 (19)	−0.00458 (4)	0.0384 (3)
H13	0.764151	0.491003	0.004454	0.046*
C14	0.70907 (11)	0.3521 (2)	−0.04669 (5)	0.0478 (4)
H14	0.760427	0.367257	−0.066546	0.057*
C15	0.63350 (13)	0.2582 (2)	−0.06005 (5)	0.0515 (4)
H15	0.632432	0.208868	−0.089015	0.062*
C16	0.55862 (11)	0.23548 (19)	−0.03116 (5)	0.0434 (4)
H16	0.506269	0.170296	−0.040539	0.052*
O2	0.12721 (6)	0.09427 (12)	0.18899 (3)	0.0358 (2)
O21	−0.07229 (7)	0.36398 (14)	0.15318 (3)	0.0444 (3)
H21	−0.064325	0.434446	0.132528	0.067*
O22	0.05992 (6)	0.47939 (13)	0.17880 (3)	0.0382 (2)
C4	−0.00572 (9)	0.38077 (16)	0.18290 (4)	0.0303 (3)
C5	−0.01891 (9)	0.27114 (18)	0.22333 (4)	0.0344 (3)
H5A	−0.043394	0.160233	0.213526	0.041*
H5B	−0.066847	0.323349	0.242898	0.041*
C6	0.19879 (11)	−0.0029 (2)	0.16834 (5)	0.0451 (4)
H6A	0.255640	0.065715	0.165358	0.068*
H6B	0.177779	−0.039210	0.138638	0.068*
H6C	0.212361	−0.102198	0.186776	0.068*
C21	0.06892 (9)	0.24303 (16)	0.25028 (4)	0.0302 (3)
C22	0.14271 (9)	0.15154 (16)	0.23166 (4)	0.0280 (3)
C23	0.22415 (9)	0.12026 (18)	0.25587 (4)	0.0338 (3)
H23	0.274312	0.058185	0.242951	0.041*
C24	0.23075 (10)	0.1813 (2)	0.29917 (4)	0.0407 (3)
H24	0.286120	0.160579	0.315982	0.049*
C25	0.15893 (11)	0.27107 (19)	0.31826 (4)	0.0422 (4)
H25	0.164426	0.311843	0.348045	0.051*
C26	0.07805 (10)	0.30186 (17)	0.29366 (4)	0.0367 (3)
H26	0.028271	0.364232	0.306810	0.044*

Comment

Acetic acid and its immediate derivatives play a crucial role in the human metabolism, e.g. in the form of activated acetic acid or acetylcholine. The introduction of the acetyl group has even been found to alter pharmacological properties such as in the case of aspirine [7, 8] where acetylation improved on the agreeableness of the salicylate prescription. In continuation of our interest in the structural versatility of carboxylic acids [9–16] the molecular and crystal structure of the title compound were determined.

According to the structure solution the compound is a derivative of acetic acid bearing a 2-methoxyphenyl substituent on its backbone. The asymmetric unit contains two complete molecules. C–O bond lengths for the methoxy group are measured at 1.4182(19) Å and 1.4193(17) Å towards the exocyclic carbon atom and 1.3642(15) Å and 1.3712(14) Å towards the endocyclic carbon atom. The latter values are in good agreement with other aromatic methoxy derivatives whose metrical parameters have been determined on grounds of diffraction studies on single crystals as found in the Cambridge Structural Database [17]. While the methoxy group seems to be in resonance with the aromatic system – apparent by the small dihedral angles of 0.00(18)° and 9.9(2)°, respectively – the acetyl groups are tilted significantly out of plane of the aromatic system they are bonded to in both molecules present in the asymmetric unit. The least-squares planes, defined by the pertaining non-hydrogen atoms of the acetyl group on the one hand and the carbon atoms of the phenyl scaffold on the other hand, enclose angles of 75.75(7) Å and 78.40(7)°, respectively. The least-squares planes defined by the non-hydrogen atoms of the two aromatic systems intersect at an angle of 49.33(7)°.

In the crystal, classical hydrogen bonds of the O–H···O type are observed next to C–H···O contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the participating atoms. The classical hydrogen bonds connect the two molecules present in the asymmetric unit to the well-known pattern of carboxylic acid dimers; however, these alone are not centrosymmetric due to the diverging orientation of the methoxy substituent towards their respective carrier phenyl moiety. Centrosymmetry is introduced into the supermolecular pattern by taking into account a) the C–H···O contacts that are supported by the hydrogen atom in *ortho* position to the acetyl substituent in the molecule whose methoxy group is tilted slightly more out-of-plane of its aromatic parent system as donor, as well as b) the keto-type oxygen atom of the carboxyl group in the other molecule present in the asymmetric unit as acceptor. The resulting assembly of four molecules as a pair of pairs features an inversion centre in the middle. In terms of graph set-analysis [18, 19], the descriptor for the classical hydrogen bonds is $R_2^2(8)$ at the binary level while the descriptor for the C–H···O contacts is $R_2^2(12)$ at the unary level. Furthermore, one could

discuss the presence of a C–H···π interaction stemming from one of the methylene group hydrogen atoms and the aromatic system of the symmetry-generated equivalent of this molecule. π Stacking is not a dominant feature in the crystal structure of the title compound with the shortest distance between two centres of gravity measured at 4.8120(9) Å.

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