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The crystal structure of α -(*meta*-methoxyphenoxy)-*ortho*-tolyllic acid, $C_{15}H_{14}O_4$

Table 1: Data collection and handling.

Crystal:	Green platelet
Size:	0.59 × 0.35 × 0.24 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.10 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	28.3°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11,956, 3185, 0.014
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2710
$N(\text{param})_{\text{refined}}$:	173
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

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Abstract

$C_{15}H_{14}O_4$, monoclinic, $C2/c$ (no. 15), $a = 27.1122(8)$ Å, $b = 6.4295(2)$ Å, $c = 14.7495(4)$ Å, $\beta = 91.7070(10)^\circ$, $V = 2569.96(13)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0387$, $wR_{\text{ref}}(F^2) = 0.1091$, $T = 200$ 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 prepared upon alkaline hydrolysis of methyl α -(*meta*-methoxyphenyl)-tolylate. Crystals suitable

for the diffraction study were obtained upon slow evaporation of a solution of the product.

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 $1.2U_{\text{eq}}(C)$.

The H atoms of the methyl group 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 $1.5U_{\text{eq}}(C)$.

The carboxylic H atom was 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 $1.5U_{\text{eq}}(O)$.

Comment

Benzoic acid has found widespread use as a ligand in coordination chemistry for a variety of transition metals and elements from the s- and p-block of the periodic system of the elements. It can act as a neutral or – upon deprotonation – an anionic ligand and serve as mono- or bidentate ligand. By varying the substituents on the phenyl moiety, the acidity of the carboxylic acid group can be fine-tuned. Particular interest rests in benzoic acid derivatives showing an asymmetric pattern of substituents on the aromatic moiety due to different possible orientations of

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.20646 (3)	−0.38416 (14)	0.57101 (6)	0.0395 (2)
H1	0.234382	−0.388608	0.551217	0.059*
O2	0.20664 (3)	−0.07355 (13)	0.50352 (6)	0.0378 (2)
O3	0.08376 (3)	0.29500 (13)	0.46669 (6)	0.0353 (2)
O4	0.19783 (3)	0.68803 (15)	0.29798 (6)	0.0449 (2)
C1	0.18548 (4)	−0.20648 (17)	0.54735 (7)	0.0285 (2)
C2	0.12336 (4)	0.15614 (17)	0.49000 (7)	0.0287 (2)
H2A	0.150146	0.232738	0.522571	0.034*
H2B	0.136890	0.095431	0.434285	0.034*
C3	0.20937 (6)	0.8607 (3)	0.24244 (12)	0.0591 (4)
H3A	0.198991	0.989451	0.271922	0.089*
H3B	0.192034	0.846998	0.183489	0.089*
H3C	0.245034	0.864906	0.233599	0.089*
C11	0.13397 (4)	−0.18336 (17)	0.57777 (7)	0.0273 (2)
C12	0.10408 (4)	−0.01430 (16)	0.54958 (7)	0.0268 (2)
C13	0.05531 (4)	−0.00951 (18)	0.57781 (8)	0.0320 (2)
H13	0.034508	0.102647	0.559433	0.038*
C14	0.03673 (4)	−0.1654 (2)	0.63214 (9)	0.0378 (3)
H14	0.003282	−0.160242	0.649467	0.045*
C15	0.06650 (5)	−0.3283 (2)	0.66127 (9)	0.0393 (3)
H15	0.053924	−0.432958	0.699727	0.047*
C16	0.11495 (4)	−0.33715 (18)	0.63374 (8)	0.0339 (3)
H16	0.135462	−0.449344	0.653214	0.041*
C21	0.09531 (4)	0.45783 (17)	0.41143 (7)	0.0297 (2)
C22	0.14201 (4)	0.49436 (17)	0.37922 (7)	0.0307 (2)
H22	0.168483	0.403126	0.394865	0.037*
C23	0.14990 (4)	0.66640 (18)	0.32354 (7)	0.0323 (2)
C24	0.11140 (5)	0.79812 (18)	0.29836 (8)	0.0366 (3)
H24	0.116592	0.912808	0.259172	0.044*
C25	0.06482 (5)	0.75787 (19)	0.33206 (8)	0.0382 (3)
H25	0.038251	0.847979	0.315656	0.046*
C26	0.05608 (4)	0.59172 (18)	0.38835 (8)	0.0344 (3)
H26	0.024130	0.568332	0.411063	0.041*

the ligand in coordination compounds and the possible formation of stereoisomeric products. In continuation of our interest in the structural diversity of carboxylic acids [7–14 & references cited therein] it seemed interesting to determine the crystal structure of the title compound to enable comparative studies. Later work will focus on a comprehensive study aimed at rationalizing the coordination behaviour of various benzoic acid derivatives towards a number of transition metals in dependence of the pH value of the reaction batches to enable comparative studies.

The molecule is essentially flat with the largest deviation of an atom from the least-squares plane defined by all non-hydrogen atoms measured at $-0.242(1)$ Å. C–O bond lengths of $1.2246(13)$ and $1.3186(13)$ Å in the carboxyl group are in good agreement with corresponding values found in

the Cambridge Structural Database [15]. C–C–C angles in the phenyl ring of the benzoic acid moiety cover a range of $117.97(10)^\circ$ – $121.26(11)^\circ$ with the smallest angle found on the carbon atom bearing the aromatic substituent. The least-squares planes defined by the non-hydrogen atoms of the carboxylic acid group and the carbon atoms of the phenyl moiety it is bonded to intersect at an angle of $7.05(13)^\circ$, while the least-squares planes defined by the respective carbon atoms of both aromatic moieties enclose an angle of $5.06(5)^\circ$.

In the crystal, carboxylic acid groups are involved in centrosymmetric hydrogen-bonded dimers, a pattern that has been the subject of a broader review recently [16]. In terms of graph-set analysis [17, 18], the descriptor for these hydrogen bonds is $R_2^2(8)$ at the unitary level. In addition, one can debate the presence of two C–H $\cdots$ π interactions that are supported by one hydrogen atom each on both phenyl moieties and invariably have the other aromatic system as acceptor. The shortest intercentroid distance between two aromatic systems was measured at $3.9462(7)$ Å and involves the two different aromatic moieties present in the molecule.

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