Crystal Structure of Ethyl 6,6'-(1,2-Ethanediy1)-4,4'-bis(trifluoromethyl)-salicylate

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The title compound, ethyl 6,6'-(1,2-ethanediy1)-4,4'-bis(trifluoromethyl)salicylate, crystallized in the triclinic sytem, space group $P\bar{1}$, with cell constants $a = 4.8296(3)\text{\AA}$, $b = 10.1649(5)\text{\AA}$, $c = 11.4127(6)\text{\AA}$, $\alpha = 108.086(2)^\circ$, $\beta = 99.641(2)^\circ$, $\gamma = 95.665(5)^\circ$, $V = 518.24(5)\text{\AA}^3$ and $Z = 1$. The molecule is almost planar, and possesses a centre of inversion. Intramolecular hydrogen bonds were found between the phenolic OH group and the carboxylic oxygen with a distance of 251.32(19) pm between the oxygen atoms.

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Functionalized trifluoromethylphenols and -salicylates represent an important class of compounds for the development of new pharmaceuticals, agrochemicals and ligands, because of the unique properties of the CF_3 group.¹ A new and easy way to obtain these trifluoromethylated arenes was found in the lewis acid-mediated formal [3+3] cyclisation reaction of 1,3-bis(silyl enol ethers) with α,β -unsaturated trifluoromethyl ketons.^{2,3}

All educts used to synthesize the title compound were prepared as described in the literature;⁴ TiCl_4 and dry solvents were used as received without further purification. Under an argon atmosphere at -78°C , TiCl_4 (0.4 mL, 3.6 mmol) was added to a solution of 1-ethoxy-1,3-bis(trimethylsilyloxy)-buta-1,3-diene^{4a} (1.48 g, 5.39 mmol) and (3Z/7Z)-4,7-diethoxy-1,1,1,10,10,10-hexafluoro-deca-3,7-diene-2,9-one^{4b} (0.6 g, 1.8 mmol) in 5 mL of dry CH_2Cl_2 . The temperature of the mixture was allowed to rise to 20°C during 14 h, followed by an aqueous workup with HCl (10%, 20 mL). After separation of the organic layer, the aqueous layer was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were dried over Na_2SO_4 , filtered and concentrated in vacuo. Purification by column chromatography (silica gel, heptane/EtOAc = 20:1) yielded the title compound as a colourless solid (350 mg, 37%). Single

crystals, suitable for X-ray analysis, were obtained by slow evaporation of a diethylether/cyclohexane (1:1) solvent mixture with a melting point of 139°C . The structure of the compound was independently verified by IR, NMR, and mass-spectral analyses.³

The crystal structure of the compound was determined using the single-crystal X-ray diffraction method. Data collection was done at 173(2)K using graphite-monochromated Mo- K_α ($\lambda = 0.71073\text{\AA}$) radiation on a Bruker X8Apex system with a CCD area detector. The structure was solved with direct methods by SHELXS97 and refined by SHELXL97.⁵ Complete data collection parameters and details of the structure solution are given in Table 1.

As a result of the x-ray investigation, half of the molecule is

Fig. 1 Chemical diagram of the title compound.

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Table 1 Crystal and experimental data

Formula: $\text{C}_{22}\text{H}_{20}\text{F}_6\text{O}_6$	
Formula weight: 494.38	
Crystal system: triclinic	
Space group: $P\bar{1}$	$Z = 1$
$a = 4.8296(3)\text{\AA}$	$\alpha = 108.086(2)^\circ$
$b = 10.1649(5)\text{\AA}$	$\beta = 99.641(2)^\circ$
$c = 11.4127(6)\text{\AA}$	$\gamma = 95.665(5)^\circ$
$V = 518.24(5)\text{\AA}^3$	
$D_x = 1.584\text{ g/cm}^3$	$D_m = \text{not measured}$
No. of reflections used = 9975	
$2\theta_{\text{max}} = 54.98^\circ$ with Mo- K_α	
$R = 0.055$	
$(\Delta\sigma)_{\text{max}} = 0.003$	
$(\Delta\rho)_{\text{max}} = 0.36\text{ e}\text{\AA}^{-3}$	
$(\Delta\rho)_{\text{min}} = -0.43\text{ e}\text{\AA}^{-3}$	
Measurement: X8Apex area detector	
Program system: Bruker SHELXTL	
Structure determination: direct methods	
Refinement: full matrix least squares on F^2	

Table 2 Selected bond lengths (Å) and bond angles (°) for the title compound

Atoms	Distance (Å)	Atoms	Angle (°)
C1-C1A	1.532(3)	C1A-C1-C2	114.57(15)
C1-C2	1.524(2)	C1-C2-C3	122.07(13)
C4-O3	1.347(2)	F1-C8-C6	112.19(15)
C8-F1	1.303(2)	C4-O3-H3	109.5
C9-O1	1.224(2)	C9-O2-C10	116.01(13)
C9-C3	1.488(2)	O1-C9-C3	123.07(15)
C9-O2	1.327(2)

Fig. 2 Chemical structure of the title compound with 50% probability for the displacement ellipsoids.

found in the asymmetric unit, which means that the molecule is almost planar. The CF_3 -moiety appears to be slightly disordered

with a ratio of about 94/6. Assuming a fixed distance of 84 pm between the hydrogen and the oxygen of the OH group, the $\text{H}\cdots\text{O}$ distance to the carboxylic oxygen is 177.2 pm, the $\text{O-H}\cdots\text{O}$ angle being 146° .

CCDC 644289 contains supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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