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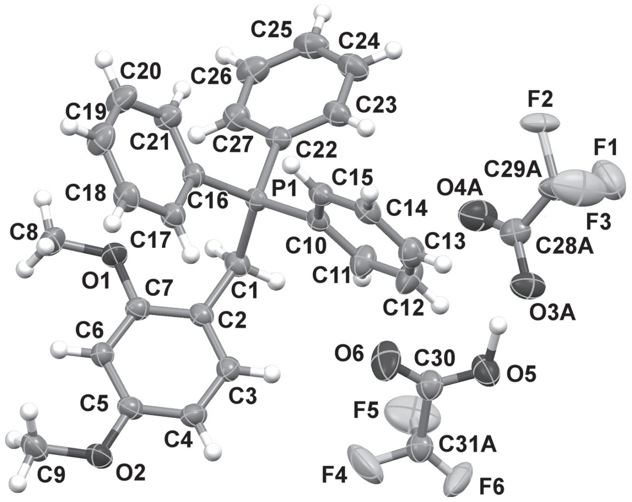
Crystal structure of (2,4-dimethoxybenzyl) triphenylphosphonium trifluoroacetate — trifluoroacetic acid (1/1), $C_{31}H_{27}F_6O_6P$



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Abstract

$C_{31}H_{27}F_6O_6P$, triclinic, $P\bar{1}$ (no. 2), $a = 8.0017(2)$ Å, $b = 11.1702(3)$ Å, $c = 17.8353(4)$ Å, $\alpha = 104.9000(10)°$, $\beta = 96.5360(10)°$, $\gamma = 97.7380(10)°$, $V = 1508.05(7)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0354$, $wR_{ref}(F^2) = 0.0896$, $T = 150(2)$ K.

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The asymmetric unit of the title crystal 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.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.40 \times 0.23 \times 0.17$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ:	1.53 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	72.37°, 94%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	49829, 5133, 0.035
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4610
$N(param)_{refined}$:	468
Programs:	Bruker [1], SHELX [2, 3], Mercury [4]

Source of material

All reagents were obtained from Sigma-Aldrich and used without further purification. 2,4-Dimethoxybenzyl alcohol (0.42 g, 2.5 mmol, 1 eq.) was added to a solution of triphenylphosphine (1.31 g, 5 mmol, 2 eq.) in dry toluene (5 mL) at 0 °C under an argon atmosphere. Trifluoroacetic acetic anhydride (0.35 mL, 2.5 mmol, 1 eq.) in dry toluene (5 mL) was subsequently added drop-wise to the reaction mixture. The reaction mixture was allowed to reach room temperature, after which it was heated to and kept at 60 °C for 16 hours. Precipitation with the addition of Et_2O (100 mL), followed by recrystallization from DCM, gave the title compound (85%, 1.10 g), as *light yellow block-like crystals*: ^{1}H-NMR (600 MHz, $CDCl_3$) δ_H [ppm] 7.78 (3H, br t, $J = 7.5$ Hz, H-4′), 7.63 (6H, ddd, $J = 7.7$, 7.5 Hz, $J_{PH} = 3.6$ Hz, H-3′ and H-5′), 7.48 (6H, br dd, $J_{PH} = 12.3$ Hz, $J = 7.7$ Hz, H-2′ and H-6′), 6.91 (1H, dd, $J = 8.4$ Hz, $J_{PH} = 2.8$ Hz, H-6), 6.33 (1H, dd, $J = 8.4$, 2.1 Hz, H-5), 6.19 (1H, d, $J = 2.1$ Hz, H-3), 4.45 (2H, d, $J_{PH} = 13.0$ Hz, -CH_2-), 3.37 (3H, s, -OMe), 3.19 (3H, s, -OMe); ^{13}C-NMR (151 MHz, $CDCl_3$) δ_C [ppm] 162.9 (d, $J_{PC} = 3.3$ Hz, C-4), 160.9 (q, $J_{FC} = 36.7$ Hz, -C=O), 158.8 (d, $J_{PC} = 4.8$ Hz, C-2), 135.7 (d, $J_{PC} = 2.5$ Hz, C-4′), 134.4 (d, $J_{PC} = 9.6$ Hz, C-2′ and C-6′), 132.8 (d, $J_{PC} = 5.4$ Hz, C-6), 130.7 (d, $J_{PC} = 12.4$ Hz, C-3′ and C-5′), 118.7 (d, $J_{PC} = 85.2$ Hz, C-1′), 116.7 (q, $J_{FC} = 290.8$ Hz, -CF_3), 107.1 (d, $J_{PC} = 8.9$ Hz, C-1), 105.7 (s, C-5), 99.0 (s, C-3), 56.0 (4-OMe), 55.3 (2-OMe), 25.6 (d, $J_{PC} = 49.5$ Hz, -CH_2-); ^{31}P-NMR (151 MHz, $CDCl_3$) δ_P [ppm] 19.7 (s, -PPh_3); ^{19}F-NMR (151 MHz, $CDCl_3$) δ_F [ppm] −81.90 (s, -CF_3); HRMS (ES): m/z $[M]^+$ required for $[C_9H_{11}O_2PPh_3]^+$: 413.1670, found 413.1663.

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

Atom	x	y	z	U_{iso}*/U_{eq}
P1	0.06949(5)	0.78918(3)	0.21772(2)	0.02632(11)
O1	0.03707(15)	1.06763(10)	0.34593(6)	0.0400(3)
O2	0.37751(16)	1.08918(11)	0.59293(6)	0.0429(3)
O5	0.75905(17)	0.33638(11)	0.31999(8)	0.0502(3)
H5	0.814(3)	0.320(2)	0.2597(15)	0.075*
O6	0.8437(2)	0.54398(13)	0.35006(10)	0.0679(4)
C1	−0.03351(19)	0.81364(15)	0.30501(9)	0.0316(3)
H1A	−0.1293	0.8590	0.2972	0.038*
H1B	−0.0828	0.7304	0.3100	0.038*
C2	0.07919(19)	0.88550(14)	0.38097(9)	0.0297(3)
C3	0.1485(2)	0.82724(15)	0.43441(9)	0.0335(3)
H3	0.1267	0.7381	0.4225	0.040*
C4	0.2484(2)	0.89640(15)	0.50453(9)	0.0366(4)
H4	0.2950	0.8552	0.5404	0.044*
C5	0.2799(2)	1.02649(15)	0.52208(9)	0.0333(3)
C6	0.2123(2)	1.08769(14)	0.47020(9)	0.0321(3)
H6	0.2344	1.1768	0.4824	0.039*
C7	0.11191(19)	1.01646(14)	0.40035(9)	0.0309(3)
C8	0.0908(3)	1.19879(17)	0.35556(12)	0.0556(5)
H8A	0.2158	1.2178	0.3635	0.083*
H8B	0.0488	1.2478	0.4013	0.083*
H8C	0.0447	1.2206	0.3085	0.083*
C9	0.4233(2)	1.22261(16)	0.60905(10)	0.0449(4)
H9A	0.4845	1.2424	0.5680	0.067*
H9B	0.4969	1.2563	0.6601	0.067*
H9C	0.3197	1.2606	0.6101	0.067*
C10	0.19682(18)	0.66755(13)	0.21458(8)	0.0277(3)
C11	0.1486(2)	0.56850(15)	0.24577(11)	0.0408(4)
H11	0.0461	0.5631	0.2678	0.049*
C12	0.2509(2)	0.47789(17)	0.24452(12)	0.0494(5)
H12	0.2185	0.4104	0.2660	0.059*
C13	0.3997(2)	0.48451(16)	0.21233(10)	0.0410(4)
H13	0.4701	0.4225	0.2126	0.049*
C14	0.4459(2)	0.58100(15)	0.17987(9)	0.0352(4)
H14	0.5474	0.5848	0.1570	0.042*
C15	0.34510(19)	0.67248(14)	0.18048(9)	0.0310(3)
H15	0.3768	0.7386	0.1577	0.037*
C16	0.20992(18)	0.92615(13)	0.21348(9)	0.0286(3)
C17	0.3580(2)	0.97019(14)	0.26932(9)	0.0331(3)
H17	0.3800	0.9302	0.3095	0.040*
C18	0.4720(2)	1.07237(15)	0.26554(11)	0.0404(4)
H18	0.5725	1.1029	0.3034	0.048*
C19	0.4399(2)	1.13031(17)	0.20663(12)	0.0469(4)
H19	0.5187	1.2004	0.2043	0.056*
C20	0.2944(2)	1.08674(17)	0.15146(12)	0.0472(4)
H20	0.2734	1.1270	0.1113	0.057*
C21	0.1787(2)	0.98458(15)	0.15435(10)	0.0366(4)
H21	0.0786	0.9546	0.1162	0.044*
C22	−0.10081(18)	0.74348(14)	0.13589(9)	0.0302(3)
C23	−0.1226(2)	0.62720(15)	0.08078(9)	0.0361(4)
H23	−0.0456	0.5708	0.0853	0.043*
C24	−0.2574(2)	0.59387(18)	0.01919(10)	0.0456(4)
H24	−0.2733	0.5140	−0.0183	0.055*
C25	−0.3689(2)	0.67595(19)	0.01180(11)	0.0471(4)
H25	−0.4599	0.6529	−0.0311	0.056*
C26	−0.3480(2)	0.79176(18)	0.06683(11)	0.0437(4)
H26	−0.4248	0.8480	0.0617	0.052*
C27	−0.2155(2)	0.82591(16)	0.12934(10)	0.0373(4)
H27	−0.2024	0.9048	0.1676	0.045*
C30	0.7771(2)	0.44883(16)	0.36147(11)	0.0400(3)
F1[a]	0.7135(8)	0.1103(5)	0.0367(3)	0.0834(16)
F2[a]	0.7951(8)	0.2615(7)	−0.0037(5)	0.0502(13)
F3[a]	0.9784(9)	0.1835(9)	0.0567(5)	0.093(3)
F4[b]	0.7305(10)	0.5663(5)	0.4853(4)	0.096(2)
F5[b]	0.5160(4)	0.4666(6)	0.40791(18)	0.0952(19)
F6[b]	0.6833(11)	0.3743(3)	0.4649(3)	0.098(2)
C29A[a]	0.8671(14)	0.2222(12)	0.0676(10)	0.0472(14)
C31A[a]	0.7242(8)	0.4582(4)	0.4419(3)	0.0400(3)
F1A[c]	0.8189(12)	0.1002(4)	0.0515(3)	0.109(2)
F2A[c]	0.8006(11)	0.2598(9)	0.0086(6)	0.105(3)
F3A[c]	1.0280(8)	0.2465(9)	0.0677(5)	0.114(3)
F4A[d]	0.6921(12)	0.5674(5)	0.4755(4)	0.098(3)
F5A[d]	0.5769(10)	0.3735(6)	0.4324(4)	0.129(5)
F6A[d]	0.8293(12)	0.4279(8)	0.4904(3)	0.135(3)
C29B[c]	0.8284(12)	0.2159(10)	0.0567(8)	0.0472(14)
C31B[c]	0.6683(7)	0.4599(4)	0.4292(3)	0.0400(3)
O3A[e]	0.87085(17)	0.26823(14)	0.19818(9)	0.0476(4)
O4A[e]	0.7084(2)	0.37043(16)	0.13586(9)	0.0637(5)
C28A[e]	0.8026(2)	0.2969(2)	0.13907(12)	0.0382(4)
O4B[f]	0.787(4)	0.344(3)	0.178(2)	0.0637(5)
O3B[f]	0.866(3)	0.152(3)	0.1747(14)	0.0476(4)
C28B[f]	0.830(5)	0.236(4)	0.148(3)	0.0382(4)

[a]Occupancy: 0.465(8), [b]Occupancy: 0.530(8), [c]Occupancy: 0.544(8), [d]Occupancy: 0.470(8), [e]Occupancy: 0.950(2), [f]Occupancy: 0.050(2).

Experimental details

The structure was solved by direct methods with the SHELXS-97 program [2], using the ShelXle [3] interface. Molecular graphics were done using ORTEP-3 [4]. All hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms. The C—H_{aromatic} and C—H_{methyl} bond distances were restrained to 0.95 Å and 0.95 Å with $U_{\mathrm{iso}}(H_{\mathrm{aromatic}}) = 1.2U_{\mathrm{eq}}$ and $U_{\mathrm{iso}}(H_{\mathrm{methyl}}) = 1.5U_{\mathrm{eq}}$ of the parent atom, respectively. The CF_3 groups appear disordered (Table 2).

Comment

Since their discovery, organic phosphonium cationic compounds have found widespread use in synthesis as phase transfer catalysts [5] and as reagents for Wittig [6] and Appel [7] reactions. In terms of biological applications, a range of phosphonium cations have also been found active as antibacterial agents against several different types of microorganisms. [8] The multi-functional use of these quaternary phosphorous compounds therefore continues to attract interest into their syntheses and applications.

The title complex crystallized in the triclinic space group $P\bar{1}$ and $Z = 2$. A single cation-anion pair, along with a hydrogen-bonded solvent molecule is contained within the asymmetric unit. The phosphonium cation exhibits a slightly distorted tetrahedral geometry with typical C—P—C bond angles of 105.69(7)° – 113.65(7)°, where both the largest and smallest angle is enclosed between the alkyl and a phenyl group. A slightly longer bond of P1—C1 = 1.8198(16) Å is observed, which corresponds to the bound alkyl group, whereas slightly shorter bonds were observed for the bound phenyl groups (1.7956(16) Å – 1.7983(15) Å). The least-squares planes defined by the carbon atoms of the phenyl moieties intersect at angles of 63.53(17)°, 63.89(16)°, and 84.16(17)°. Interestingly, face-to-face π–π interactions between the 2,4-dimethoxyarene ring systems is observed with a centroid-to-centroid distance of 3.631 Å. In addition, alternating edge-to-edge π–π interactions are observed between the same ring systems at a distance of 5.089 Å, at an angle of ca. 46.9°. The disordered moiety of the trifluoroacetato anion forms a strong O5—H5···O3 hydrogen bond (H5—O3 = 2.429 Å), at an angle of ca. 155°. The fluorine atoms of the CF_3-group of both the acetate and acetic acid molecules are disordered over two unique positions which have been modelled with occupation factors of 0.456 and 0.530, respectively. All other geometric parameters are within the expected ranges.

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