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(2,4-Dihydroxybenzylidene)dimethylammonium dichlorophosphinate

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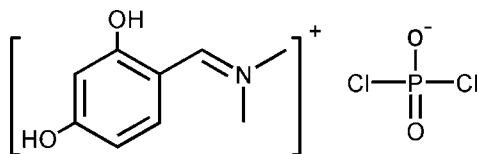
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.043; wR factor = 0.116; data-to-parameter ratio = 18.7.

In the title compound, $\text{C}_9\text{H}_{12}\text{NO}_2^+\cdot\text{Cl}_2\text{PO}_2^-$, the molecular skeleton of the cation is nearly planar with an r.m.s. deviation of 0.0336 Å. In the crystal structure, intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds link cations and anions into chains running along $[1\bar{1}0]$.

Related literature

For details of the synthesis, see Ramadas & David Krupadanam (2000). For typical values of $\text{C}=\text{N}$ bond lengths, see Elmah *et al.* (1999).



Experimental

Crystal data

$\text{C}_9\text{H}_{12}\text{NO}_2^+\cdot\text{Cl}_2\text{O}_2\text{P}^-$
 $M_r = 300.07$

Triclinic, $P\bar{1}$
 $a = 7.922$ (4) Å

$b = 8.163$ (4) Å
 $c = 11.035$ (9) Å
 $\alpha = 100.021$ (19)°
 $\beta = 107.035$ (2)°
 $\gamma = 103.02$ (3)°
 $V = 642.3$ (7) Å³

$Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.63$ mm⁻¹
 $T = 293$ (2) K
 $0.20 \times 0.20 \times 0.20$ mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2005)
 $T_{\text{min}} = 0.903$, $T_{\text{max}} = 1.000$
(expected range = 0.796–0.881)

6473 measured reflections
2898 independent reflections
2374 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.116$
 $S = 1.06$
2898 reflections

155 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.34$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.38$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{O1}-\text{H1A}\cdots\text{O4}^{\text{i}}$ | 0.82 | 1.79 | 2.609 (3) | 180 |
| $\text{O2}-\text{H2}\cdots\text{O3}^{\text{ii}}$ | 0.82 | 1.83 | 2.635 (3) | 167 |

Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y + 2, -z + 1$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

HJX acknowledges a Start-up Grant from Southeast University, People's Republic of China.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2507).

References

- Elmah, A., Kabak, M. & Elerman, Y. (1999). *J. Mol. Struct.* **484**, 229–234.
Ramadas, S. & David Krupadanam, G. L. (2000). *Tetrahedron Asymmetry*, **11**, 3375–3393.
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supplementary materials

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(2,4-Dihydroxybenzylidene)dimethylammonium dichlorophosphate

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Comment

Vilsmeier conditions are important synthetic tool usually utilized in the synthesis of aldehydes. The title compound is a Vilsmeier intermediate synthesized from resorcinol, DMF and POCl₃ in dry CH₃CN. Here we report its crystal structure.

In the title compound (Fig. 1), all bond lengths are normal. The C7=N1 bond length of 1.288 (3) Å indicates a high degree of double-bond character comparable with the typical values of C=N bond length (Elmah *et al.*, 1999). The two P—O bond lengths are almost equal - 1.4604 (19) and 1.4642 (18) Å, respectively.

In the crystal, the cations and anions are further connected via O—H...O hydrogen bonds into chains running in direction [1-10].

Experimental

All chemicals were obtained from commercial sources and used without further purification except POCl₃ and DMF, which were distilled under reduced pressure before use. The title compound was prepared according to the literature (Ramadas & David Krupadanam, 2000).

Refinement

All H atoms were geometrically positioned (C—H 0.93-0.96 Å, O—H 0.82 Å) and allowed to ride on the parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2-1.5 U_{\text{eq}}(\text{C}, \text{O})$.

Figures

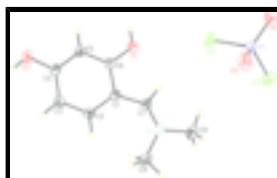


Fig. 1. A view of the title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

(2,4-Dihydroxybenzylidene)dimethylammonium dichlorophosphate

Crystal data

C₉H₁₂NO₂⁺·Cl₂O₂P⁻

$M_r = 300.07$

Triclinic, $P\bar{1}$

$Z = 2$

$F_{000} = 308$

$D_x = 1.552 \text{ Mg m}^{-3}$

supplementary materials

Hall symbol: -P 1

$a = 7.922$ (4) Å

$b = 8.163$ (4) Å

$c = 11.035$ (9) Å

$\alpha = 100.021$ (19)°

$\beta = 107.035$ (2)°

$\gamma = 103.02$ (3)°

$V = 642.3$ (7) Å³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1854 reflections

$\theta = 2.7$ – 27.5 °

$\mu = 0.63$ mm⁻¹

$T = 293$ (2) K

Prism, colourless

$0.20 \times 0.20 \times 0.20$ mm

Data collection

Rigaku Mercury2
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 13.6612 pixels mm⁻¹

$T = 293$ (2) K

ω scans

Absorption correction: multi-scan
(CrystalClear; Rigaku, 2005)

$T_{\min} = 0.903$, $T_{\max} = 1.000$

6473 measured reflections

2898 independent reflections

2374 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

$\theta_{\text{max}} = 27.5$ °

$\theta_{\text{min}} = 2.7$ °

$h = -10 \rightarrow 10$

$k = -10 \rightarrow 10$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.043$

$wR(F^2) = 0.116$

$S = 1.06$

2898 reflections

155 parameters

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2 + 0.2201P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.34$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.38$ e Å⁻³

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -

factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|---------------|--------------|--------------|----------------------------------|
| P1 | 0.07808 (7) | 0.57775 (7) | 0.79425 (5) | 0.04024 (16) |
| Cl2 | -0.01734 (10) | 0.66505 (10) | 0.63397 (6) | 0.0665 (2) |
| O1 | 0.1067 (2) | 0.88448 (19) | 0.41735 (15) | 0.0469 (4) |
| H1A | 0.0823 | 0.7961 | 0.3592 | 0.070* |
| O2 | 0.4455 (2) | 1.1302 (2) | 0.17313 (15) | 0.0556 (4) |
| H2 | 0.5384 | 1.2072 | 0.1825 | 0.083* |
| C1 | 0.3561 (2) | 1.1426 (2) | 0.52665 (18) | 0.0340 (4) |
| N1 | 0.3863 (2) | 1.2128 (2) | 0.76201 (16) | 0.0424 (4) |
| C6 | 0.2445 (3) | 1.0094 (2) | 0.40992 (19) | 0.0342 (4) |
| C5 | 0.2758 (3) | 1.0099 (3) | 0.29337 (19) | 0.0382 (4) |
| H5A | 0.2007 | 0.9231 | 0.2179 | 0.046* |
| C7 | 0.3111 (3) | 1.1237 (3) | 0.6409 (2) | 0.0394 (4) |
| H7A | 0.2087 | 1.0299 | 0.6251 | 0.047* |
| C3 | 0.5312 (3) | 1.2722 (3) | 0.4014 (2) | 0.0424 (5) |
| H3A | 0.6267 | 1.3596 | 0.3980 | 0.051* |
| C4 | 0.4190 (3) | 1.1396 (3) | 0.28853 (19) | 0.0388 (4) |
| C2 | 0.4993 (3) | 1.2723 (3) | 0.5167 (2) | 0.0411 (5) |
| H2A | 0.5746 | 1.3609 | 0.5911 | 0.049* |
| C8 | 0.5515 (4) | 1.3646 (4) | 0.8156 (2) | 0.0627 (7) |
| H8A | 0.5790 | 1.4070 | 0.9081 | 0.094* |
| H8B | 0.5293 | 1.4545 | 0.7729 | 0.094* |
| H8C | 0.6541 | 1.3315 | 0.8009 | 0.094* |
| C9 | 0.3073 (4) | 1.1623 (4) | 0.8600 (2) | 0.0642 (7) |
| H9A | 0.2007 | 1.0624 | 0.8178 | 0.096* |
| H9B | 0.2720 | 1.2571 | 0.8998 | 0.096* |
| H9C | 0.3977 | 1.1345 | 0.9261 | 0.096* |
| Cl1 | 0.00162 (13) | 0.72157 (11) | 0.92482 (8) | 0.0820 (3) |
| O4 | -0.0294 (3) | 0.3961 (2) | 0.76791 (18) | 0.0643 (5) |
| O3 | 0.2793 (2) | 0.6276 (3) | 0.83673 (19) | 0.0676 (5) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|-------------|------------|------------|
| P1 | 0.0420 (3) | 0.0381 (3) | 0.0372 (3) | 0.0040 (2) | 0.0153 (2) | 0.0083 (2) |
| Cl2 | 0.0797 (5) | 0.0756 (5) | 0.0469 (4) | 0.0299 (4) | 0.0158 (3) | 0.0234 (3) |
| O1 | 0.0444 (8) | 0.0444 (8) | 0.0439 (8) | -0.0018 (6) | 0.0192 (7) | 0.0040 (6) |
| O2 | 0.0622 (11) | 0.0637 (11) | 0.0367 (8) | 0.0029 (8) | 0.0235 (7) | 0.0116 (7) |
| C1 | 0.0336 (9) | 0.0374 (10) | 0.0300 (9) | 0.0116 (8) | 0.0087 (7) | 0.0087 (7) |
| N1 | 0.0439 (10) | 0.0527 (11) | 0.0315 (9) | 0.0174 (8) | 0.0129 (7) | 0.0091 (7) |
| C6 | 0.0322 (9) | 0.0349 (9) | 0.0357 (10) | 0.0108 (7) | 0.0110 (7) | 0.0096 (7) |
| C5 | 0.0402 (10) | 0.0382 (10) | 0.0320 (10) | 0.0094 (8) | 0.0104 (8) | 0.0047 (8) |
| C7 | 0.0376 (10) | 0.0439 (11) | 0.0362 (10) | 0.0121 (8) | 0.0121 (8) | 0.0098 (8) |

supplementary materials

| | | | | | | |
|-----|-------------|-------------|-------------|-------------|-------------|--------------|
| C3 | 0.0410 (11) | 0.0408 (11) | 0.0406 (11) | 0.0031 (8) | 0.0132 (9) | 0.0121 (9) |
| C4 | 0.0427 (11) | 0.0439 (11) | 0.0323 (10) | 0.0138 (8) | 0.0137 (8) | 0.0133 (8) |
| C2 | 0.0402 (11) | 0.0395 (10) | 0.0349 (10) | 0.0050 (8) | 0.0074 (8) | 0.0067 (8) |
| C8 | 0.0578 (15) | 0.0714 (17) | 0.0398 (13) | 0.0026 (12) | 0.0120 (11) | -0.0034 (11) |
| C9 | 0.0794 (18) | 0.0802 (18) | 0.0377 (12) | 0.0198 (14) | 0.0290 (12) | 0.0162 (12) |
| Cl1 | 0.1114 (7) | 0.0773 (5) | 0.0594 (4) | 0.0271 (4) | 0.0444 (4) | -0.0020 (3) |
| O4 | 0.0824 (13) | 0.0392 (9) | 0.0644 (12) | -0.0028 (8) | 0.0353 (10) | 0.0061 (8) |
| O3 | 0.0420 (9) | 0.0902 (14) | 0.0699 (12) | 0.0091 (9) | 0.0166 (8) | 0.0371 (10) |

Geometric parameters (Å, °)

| | | | |
|------------|-------------|------------|-------------|
| P1—O3 | 1.4598 (19) | C6—C5 | 1.380 (3) |
| P1—O4 | 1.4641 (18) | C5—C4 | 1.387 (3) |
| P1—Cl1 | 2.0160 (13) | C5—H5A | 0.9300 |
| P1—Cl2 | 2.0262 (15) | C7—H7A | 0.9300 |
| O1—C6 | 1.349 (2) | C3—C2 | 1.367 (3) |
| O1—H1A | 0.8200 | C3—C4 | 1.401 (3) |
| O2—C4 | 1.342 (3) | C3—H3A | 0.9300 |
| O2—H2 | 0.8200 | C2—H2A | 0.9300 |
| C1—C2 | 1.412 (3) | C8—H8A | 0.9600 |
| C1—C6 | 1.426 (3) | C8—H8B | 0.9600 |
| C1—C7 | 1.431 (3) | C8—H8C | 0.9600 |
| N1—C7 | 1.292 (3) | C9—H9A | 0.9600 |
| N1—C8 | 1.470 (3) | C9—H9B | 0.9600 |
| N1—C9 | 1.471 (3) | C9—H9C | 0.9600 |
| O3—P1—O4 | 120.75 (12) | C1—C7—H7A | 114.0 |
| O3—P1—Cl1 | 109.16 (10) | C2—C3—C4 | 119.5 (2) |
| O4—P1—Cl1 | 107.38 (8) | C2—C3—H3A | 120.2 |
| O3—P1—Cl2 | 108.40 (8) | C4—C3—H3A | 120.2 |
| O4—P1—Cl2 | 108.48 (9) | O2—C4—C5 | 117.32 (18) |
| Cl1—P1—Cl2 | 100.85 (7) | O2—C4—C3 | 122.41 (19) |
| C6—O1—H1A | 109.5 | C5—C4—C3 | 120.26 (19) |
| C4—O2—H2 | 109.5 | C3—C2—C1 | 122.27 (18) |
| C2—C1—C6 | 116.78 (18) | C3—C2—H2A | 118.9 |
| C2—C1—C7 | 128.16 (18) | C1—C2—H2A | 118.9 |
| C6—C1—C7 | 115.03 (18) | N1—C8—H8A | 109.5 |
| C7—N1—C8 | 125.83 (19) | N1—C8—H8B | 109.5 |
| C7—N1—C9 | 119.8 (2) | H8A—C8—H8B | 109.5 |
| C8—N1—C9 | 114.33 (19) | N1—C8—H8C | 109.5 |
| O1—C6—C5 | 121.34 (17) | H8A—C8—H8C | 109.5 |
| O1—C6—C1 | 117.69 (17) | H8B—C8—H8C | 109.5 |
| C5—C6—C1 | 120.97 (18) | N1—C9—H9A | 109.5 |
| C6—C5—C4 | 120.18 (18) | N1—C9—H9B | 109.5 |
| C6—C5—H5A | 119.9 | H9A—C9—H9B | 109.5 |
| C4—C5—H5A | 119.9 | N1—C9—H9C | 109.5 |
| N1—C7—C1 | 131.9 (2) | H9A—C9—H9C | 109.5 |
| N1—C7—H7A | 114.0 | H9B—C9—H9C | 109.5 |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H··· <i>A</i> | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|--------------------------|-------------|---------------|-----------------------|-------------------------|
| O1—H1A···O4 ⁱ | 0.82 | 1.79 | 2.609 (3) | 180 |
| O2—H2···O3 ⁱⁱ | 0.82 | 1.83 | 2.635 (3) | 167 |

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x+1, -y+2, -z+1$.

Fig. 1

