| | | | | |
|---|---|---|---|---|
| C(3) | 0.3536 (10) | 1.1787 (5) | 0.2414 (3) | 0.041 (2) |
| C(4) | 0.4805 (10) | 1.2099 (5) | 0.3019 (3) | 0.044 (2) |
| C(5) | 0.2336 (10) | 0.9459 (6) | 0.4251 (4) | 0.049 (3) |
| C(6) | 0.6269 (10) | 1.3088 (6) | 0.3008 (4) | 0.049 (3) |
| C(7) | 0.0897 (10) | 1.0087 (5) | 0.2296 (4) | 0.038 (2) |
| C(8) | −0.1108 (11) | 0.9839 (5) | 0.2672 (4) | 0.052 (3) |
| C(9) | −0.2498 (12) | 0.9257 (6) | 0.2234 (5) | 0.072 (3) |
| C(10) | −0.1864 (14) | 0.8898 (7) | 0.1401 (6) | 0.076 (4) |
| C(11) | 0.0112 (15) | 0.9130 (6) | 0.1009 (4) | 0.069 (3) |
| C(12) | 0.1513 (11) | 0.9718 (5) | 0.1448 (4) | 0.056 (3) |
| C(13) | 0.3450 (12) | 1.2437 (5) | 0.1545 (4) | 0.047 (3) |
| C(14) | 0.1602 (11) | 1.2915 (5) | 0.1326 (4) | 0.054 (3) |
| C(15) | 0.1515 (13) | 1.3512 (6) | 0.0513 (5) | 0.068 (3) |
| C(16) | 0.3280 (15) | 1.3618 (7) | −0.0060 (4) | 0.074 (4) |
| C(17) | 0.5133 (14) | 1.3142 (7) | 0.0142 (4) | 0.076 (3) |
| C(18) | 0.5244 (11) | 1.2542 (6) | 0.0947 (4) | 0.060 (3) |
| C(19) | −0.2098 (12) | 0.6445 (6) | 0.5015 (4) | 0.050 (3) |
| C(20) | −0.3436 (11) | 0.6888 (6) | 0.4351 (4) | 0.076 (3) |
| C(21) | −0.0672 (12) | 0.4413 (6) | 0.7393 (4) | 0.056 (3) |
| C(22) | −0.2501 (12) | 0.3625 (6) | 0.7625 (4) | 0.078 (3) |

Table 2. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| N(1)—C(1) | 1.363 (8) | N(1)—C(4) | 1.382 (7) |
| O(1)—C(5) | 1.208 (8) | O(2)—C(5) | 1.312 (8) |
| O(3)—C(6) | 1.229 (7) | O(4)—C(6) | 1.324 (8) |
| O(5)—C(19) | 1.200 (10) | O(6)—C(19) | 1.332 (7) |
| O(7)—C(21) | 1.228 (7) | O(8)—C(21) | 1.313 (9) |
| C(1)—C(2) | 1.405 (8) | C(1)—C(5) | 1.477 (8) |
| C(2)—C(3) | 1.404 (8) | C(2)—C(7) | 1.473 (9) |
| C(3)—C(4) | 1.393 (9) | C(3)—C(13) | 1.499 (8) |
| C(4)—C(6) | 1.436 (9) | C(7)—C(8) | 1.375 (9) |
| C(19)—C(20) | 1.490 (10) | C(21)—C(22) | 1.465 (10) |
| C(1)—N(1)—C(4) | 109.0 (5) | N(1)—C(1)—C(2) | 108.8 (5) |
| N(1)—C(1)—C(5) | 117.2 (5) | C(2)—C(1)—C(5) | 133.9 (6) |
| C(1)—C(2)—C(3) | 106.2 (5) | C(1)—C(2)—C(7) | 128.3 (5) |
| C(3)—C(2)—C(7) | 125.5 (5) | C(2)—C(3)—C(4) | 108.3 (5) |
| C(2)—C(3)—C(13) | 125.6 (6) | C(4)—C(3)—C(13) | 126.1 (5) |
| N(1)—C(4)—C(3) | 107.6 (5) | N(1)—C(4)—C(6) | 121.2 (5) |
| C(3)—C(4)—C(6) | 131.2 (5) | O(1)—C(5)—O(2) | 124.6 (5) |
| O(1)—C(5)—C(1) | 122.3 (6) | O(2)—C(5)—C(1) | 113.1 (5) |
| O(3)—C(6)—O(4) | 123.0 (6) | O(3)—C(6)—C(4) | 123.5 (6) |
| O(4)—C(6)—C(4) | 113.5 (5) | C(2)—C(7)—C(8) | 122.0 (5) |
| C(2)—C(7)—C(12) | 120.0 (6) | C(8)—C(7)—C(12) | 118.0 (6) |
| C(7)—C(12)—C(11) | 120.2 (6) | C(3)—C(13)—C(14) | 120.4 (6) |
| C(3)—C(13)—C(18) | 120.5 (6) | C(14)—C(13)—C(18) | 119.1 (5) |
| O(5)—C(19)—O(6) | 121.9 (6) | O(5)—C(19)—C(20) | 126.4 (6) |
| O(6)—C(19)—C(20) | 111.6 (6) | O(7)—C(21)—O(8) | 120.8 (6) |
| O(7)—C(21)—C(22) | 123.5 (7) | O(8)—C(21)—C(22) | 115.7 (5) |

Data collection, structure solution and refinement, and preparation of drawings were performed using *SHELXTL-Plus* programs (Sheldrick, 1991).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1169). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Diethyl (1-Hydroxy-2-butynyl)phosphonate

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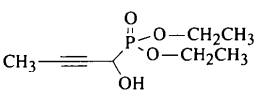
## Abstract

The structure of diethyl (1-hydroxy-2-butynyl)phosphonate, $C_8H_{15}O_4P$, exhibits nearly tetrahedral geometry around the P atom, in addition to intermolecular and intramolecular hydrogen bonding between the hydroxy group and the double-bonded phosphoryl O atom (O—H···O=P).

## Comment

Mono- and difluorinated compounds of phosphorus and their derivatives have found use as markers in many biological phosphate systems (Blackburn, Brown, Martin & Parratt, 1987; Halazy & Gross-Berges, 1992). In the course of our studies on the regiospecific fluorination of hydroxy phosphonates, the title compound, (1), was isolated (Sanders & Hammond, 1993).




(1)

Analysis of the structural data indicates that the P—O distances [1.557 (6) and 1.571 (5) Å] in the P—O—C linkages (Fig. 1) differ by 0.014 Å, but the bond distances are compatible with known values: a P—O bond distance of 1.586 Å in substituted dioxaphosphocine (Naidu, Krishnaiah & Sivakumar, 1992) and P—

O bond distances of 1.554 and 1.557 Å in diphenylphosphate (Jones, Kirby & Parker, 1992). The P—C and the P═O bond distances are compatible with literature values for similar systems (Sawka-Dobrowolska & Rulko, 1987; Golen, 1993). As in similar systems, short C—C bond distances [1.336 (14) and 1.385 (18) Å], along with high thermal motion, were noted for the ethyl C atoms (Hazel & Collin, 1972; Ezra & Collin, 1973). The geometry around the P atom is nearly tetrahedral, with angles ranging from 101.2 (4) to 116.9 (3)°.

The intramolecular O(3)—H···O(4)—P(1) hydrogen-bonding distance is 3.245 (10) Å, while the intermolecular O(3)—H···O(4*A*)—P(1*A*) hydrogen-bonding distance between adjacent molecules (Fig. 2) is 2.696 (8) Å. These distances suggest that dimers are more favored than individual molecules. The intermolecular hydrogen-bonding value is compatible with the literature value of 2.70 Å.

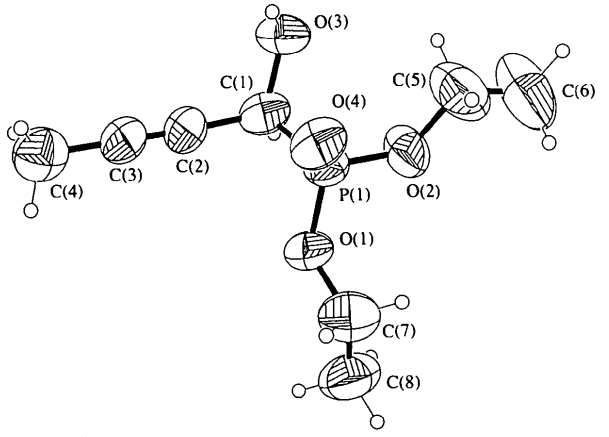



Fig. 1. A view of $(C_2H_5O)_2P(O)CH(OH)CCCH_3$ showing the labeling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

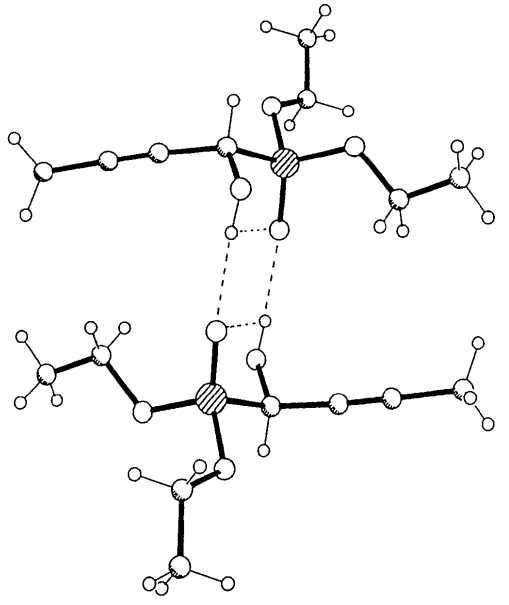


Fig. 2. A view of two adjacent $(C_2H_5O)_2P(O)CH(OH)CCCH_3$ molecules illustrating potential sites for hydrogen bonding.

## Experimental

The title compound crystallized from ethyl acetate/hexane solution to yield colorless plate-like crystals of marginal quality which were mounted on glass fibers with epoxy. Crystals of the title compound exhibited rather broad peak profiles. The best crystal from a sample of marginal crystals was chosen for further study.

*Crystal data*

| | |
|---|---|
| $C_8H_{15}O_4P$ | Mo $K\alpha$ radiation |
| $M_r$ = 206.2 | $\lambda$ = 0.71073 Å |
| Triclinic | Cell parameters from 25 reflections |
| $P\bar{1}$ | $\theta$ = 12.0–12.5° |
| $a$ = 7.668 (2) Å | $\mu$ = 0.232 $mm^{-1}$ |
| $b$ = 8.997 (1) Å | $T$ = 296 K |
| $c$ = 9.010 (2) Å | Plate |
| $\alpha$ = 115.75 (2)° | 0.40 × 0.40 × 0.18 mm |
| $\beta$ = 91.32 (2)° | Colorless |
| $\gamma$ = 97.45 (2)° | |
| $V$ = 553.0 (2) $Å^3$ | |
| $Z$ = 2 | |
| $D_x$ = 1.238 Mg $m^{-3}$ | |
| $D_m$ not measured | |

*Data collection*

| | |
|---|---|
| Nicolet Siemens *R3m/V* diffractometer | $R_{int}$ = 0.0219 |
| $\omega$ scans | $\theta_{max}$ = 25.0° |
| Absorption correction: none | $h = -1 \rightarrow 9$ |
| 2329 measured reflections | $k = -9 \rightarrow 9$ |
| 1870 independent reflections | $l = -10 \rightarrow 10$ |
| 978 observed reflections [$F > 4\sigma(F)$] | 3 standard reflections monitored every 97 reflections |
| | intensity decay: 4.5% |

*Refinement*

| | |
|---|---|
| Refinement on $F$ | $w = 1/[\sigma^2(F) + 0.0008F^2]$ |
| $R$ = 0.075 | $(\Delta/\sigma)_{max} < 0.001$ |
| $wR$ = 0.089 | $\Delta\rho_{max}$ = 0.49 e $Å^{-3}$ |
| $S$ = 1.76 | $\Delta\rho_{min}$ = −0.33 e $Å^{-3}$ |
| 978 reflections | Extinction correction: none |
| 118 parameters | Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1990) |
| H atoms refined as riding with fixed isotropic $U$ | |

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| P(1) | 0.4651 (3) | 0.6214 (2) | 0.3010 (2) | 0.061 (1) |
| O(1) | 0.5066 (7) | 0.7741 (6) | 0.2619 (6) | 0.076 (3) |
| O(2) | 0.3297 (8) | 0.4952 (6) | 0.1525 (5) | 0.082 (3) |
| O(3) | 0.6477 (7) | 0.3754 (5) | 0.2545 (5) | 0.075 (2) |

| | | | | |
|---|---|---|---|---|
| O(4) | 0.4061 (7) | 0.6544 (6) | 0.4638 (5) | 0.073 (2) |
| C(1) | 0.6712 (11) | 0.5381 (9) | 0.2628 (8) | 0.066 (4) |
| C(2) | 0.8148 (11) | 0.6577 (10) | 0.3849 (9) | 0.062 (4) |
| C(3) | 0.9219 (11) | 0.7466 (10) | 0.4847 (10) | 0.066 (4) |
| C(4) | 1.0608 (10) | 0.8626 (10) | 0.6133 (10) | 0.090 (5) |
| C(5) | 0.2039 (15) | 0.3711 (12) | 0.1679 (12) | 0.133 (7) |
| C(6) | 0.0892 (16) | 0.2810 (13) | 0.0353 (12) | 0.150 (7) |
| C(7) | 0.3750 (14) | 0.8789 (12) | 0.2718 (12) | 0.111 (6) |
| C(8) | 0.4043 (14) | 0.9587 (11) | 0.1714 (12) | 0.112 (6) |

Table 2. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| P(1)—O(1) | 1.557 (6) | P(1)—O(2) | 1.571 (5) |
| P(1)—O(4) | 1.460 (5) | P(1)—C(1) | 1.813 (9) |
| O(1)—C(7) | 1.447 (13) | O(2)—C(5) | 1.435 (13) |
| O(3)—C(1) | 1.420 (10) | C(1)—C(2) | 1.479 (9) |
| C(2)—C(3) | 1.138 (10) | C(3)—C(4) | 1.473 (10) |
| C(5)—C(6) | 1.336 (14) | C(7)—C(8) | 1.385 (18) |
| O(1)—P(1)—O(2) | 103.2 (3) | O(1)—P(1)—O(4) | 116.9 (3) |
| O(2)—P(1)—O(4) | 114.2 (3) | O(1)—P(1)—C(1) | 101.2 (4) |
| O(2)—P(1)—C(1) | 105.5 (3) | O(4)—P(1)—C(1) | 114.1 (4) |
| P(1)—O(1)—C(7) | 121.1 (6) | P(1)—O(2)—C(5) | 121.7 (6) |
| P(1)—C(1)—O(3) | 110.0 (5) | P(1)—C(1)—C(2) | 110.3 (5) |
| O(3)—C(1)—C(2) | 114.8 (7) | C(1)—C(2)—C(3) | 176.2 (10) |
| C(2)—C(3)—C(4) | 179.5 (10) | O(2)—C(5)—C(6) | 114.8 (1) |
| O(1)—C(7)—C(8) | 112.2 (9) | | |
| O(2)—P(1)—O(1)—C(7) | 69.3 (6) | O(4)—P(1)—O(1)—C(7) | −56.9 (6) |
| C(1)—P(1)—O(1)—C(7) | 178.4 (5) | O(1)—P(1)—O(2)—C(5) | −154.2 (7) |
| O(4)—P(1)—O(2)—C(5) | −26.2 (8) | C(1)—P(1)—O(2)—C(5) | 99.9 (7) |
| O(1)—P(1)—C(1)—O(3) | −166.5 (4) | O(2)—P(1)—C(1)—O(3) | −59.2 (5) |
| O(1)—P(1)—C(1)—C(2) | 65.9 (7) | O(2)—P(1)—C(1)—C(2) | 173.2 (6) |
| O(4)—P(1)—C(1)—O(3) | 67.0 (5) | P(1)—O(1)—C(7)—C(8) | −154.7 (5) |
| O(4)—P(1)—C(1)—C(2) | −60.6 (7) | P(1)—C(1)—C(2)—C(3) | 79.6 (15) |
| P(1)—O(2)—C(5)—C(6) | 175.3 (8) | C(1)—C(2)—C(3)—C(4) | −161 (10) |
| O(3)—C(1)—C(2)—C(3) | −45.3 (15) | | |

*SHELXTL-Plus* (Sheldrick, 1990) was used for data collection, structure solution by direct methods, structure refinement and the molecular drawings.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1035). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# (2*R*,3*R*,5*S*,6*S*)-2,3-Diethoxy-5,6-bis(hydroxymethyl)-2,3-dimethyl-1,4-dioxane

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## Abstract

The title compound, $C_{12}H_{24}O_6$, was synthesized and subjected to an X-ray structure determination. The aim of this structure analysis was to determine the relative orientation of two vicinal ethoxy groups in its precursor, diethyl (2*R*,3*R*,5*R*,6*R*)-5,6-diethoxy-5,6-dimethyl-1,4-dioxane-2,3-dicarboxylate, from which the title compound can be generated by a reaction that retains the absolute configuration of the molecular skeleton.

## Comment

Transacetalization of diethyl tartrate, (I), with 3,3-diethoxybutan-2-one, (II), resulted diethyl (2*R*,3*R*,5*R*,6*R*)-5,6-diethoxy-5,6-dimethyl-1,4-dioxane-2,3-dicarboxylate, (III) (Berens, 1993). A structural alternative to (III) is its isomer (V). Taking into account the possible role of the anomeric effect, (V) may be somewhat higher in energy than the isomer with both ethoxy groups in axial positions (Ley, Woods & Zanotti-Gerosa, 1992; Ley, Priepke & Warriner, 1994). According to quantum-chemical calculations by the semiempirical AM1 (Dewar, Zoebisch, Healy & Stewart, 1985) and the PM3 methods (Stewart, 1989*a*,*b*), (III) is indeed energetically more favourable than (V). However, the energy differences are small [$H_f(5) - H_f(3)$: AM1 3.8 kcal mol$^{-1}$, PM3 2.1 kcal mol$^{-1}$] and probably comparable to those between different conformers of each diastereomer. Therefore, our computational results do not allow the exclusion of one of the diastereomers from our considerations. Moreover, it was not possible to rule out (V) by means of NMR data and all attempts to crystallize the product met with failure. Thus, we reduced (III) to obtain the title compound, (IV), in the form of colourless needles. Since the reaction linking