

## Disodium D-3-Phosphoglycerate, a Substrate to Phosphoglycerate Kinase

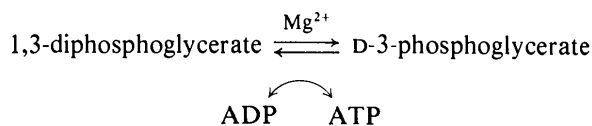
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**Abstract.**  $C_3H_5O_7P^{2-} \cdot 2Na^+$ , monoclinic,  $P2_1$ ,  $a = 9.794$  (6),  $b = 5.019$  (10),  $c = 7.799$  (8) Å,  $\beta = 111.63$  (5)°,  $Z = 2$ ,  $D_m = 2.001$  (9),  $D_x = 2.143$  (4) Mg m<sup>-3</sup>;  $R = 0.063$  for 1146 reflections. Bond lengths and angles are typical of expected values. Two intermolecular hydrogen bonds occur and one of these H atoms is also involved in a weak intramolecular hydrogen bond. The structure is compared with cadmium D-3-phosphoglycerate trihydrate which is not isostructural.

**Introduction.** The molecular configuration of D-3-phosphoglycerate is important in the interpretation of the glycolytic reaction:



which is catalysed by phosphoglycerate kinase. The structure of this enzyme has been determined to 2.5 Å resolution by Banks *et al.* (1979), but the enzyme undergoes large conformational changes when 3-phosphoglycerate is bound. Thus the location of its binding site is not straightforward and therefore the mode of phosphoryl transfer is difficult to predict.

Crystals grew over a period of 6 months by diffusion of ethanol vapour into water saturated with disodium D-3-phosphoglycerate [Sigma Chemical Co., London (lot 51C 5040)].

Preliminary diffraction photographs showed the space group to be  $P2_1$ . X-ray intensities were collected on a Stoe four-circle diffractometer by the  $\omega$ -scan technique with balanced filters and Mo  $K\alpha$  radiation within the range  $0 < \theta < 30^\circ$ . Three standard reflections were measured every 30 reflections to assess the stability of the system. 13 reflections too weak to be measured, with  $I < \sigma(I)$ , were included at their most probable value (Hamilton, 1955), and all the reflections were corrected for Lorentz and polarization factors. No correction was made for absorption [ $\mu(\text{Mo } K\alpha) = 0.49 \text{ mm}^{-1}$ ].

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The positions of two Na<sup>+</sup> cations and the phosphate group were determined from a sharpened Patterson synthesis, after the intensities were adjusted to an approximate absolute scale (Wilson, 1942). The atom coordinates, isotropic thermal parameters and overall scale factor were refined by least squares with unit weights (Sheldrick, 1975), and an electron density map indicated the remaining non-hydrogen atoms. A difference synthesis with all the non-hydrogen atoms indicated deviations from isotropic thermal vibrations and the positions of the five H atoms. The refinement converged at  $R = 0.063$ , with anisotropic thermal parameters, except for the H atoms ( $U = 0.05 \text{ \AA}^2$ ). No extinction was evident from comparison of  $|F_o|$  and  $|F_c|$ . The scattering factors were obtained from Cromer & Liberman (1970). The final atomic coordinates are given in Table 1.†

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36338 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ( $\times 10^4$ , except for H atoms  $\times 10^3$ ), and  $U_{eq}$  values ( $\times 10^3 \text{ \AA}^2$ )

	$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + 2U_{13} \cos \beta)$			
	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
P	2326 (1)	0	2344 (2)	11 (1)
O(1)	1292 (5)	1771 (12)	7007 (6)	20 (4)
O(2)	1854 (6)	-2496 (13)	7126 (9)	29 (5)
O(3)	4075 (5)	3322 (12)	7987 (7)	21 (4)
O(4)	2999 (5)	1193 (11)	4359 (6)	20 (4)
O(5)	952 (4)	1514 (11)	1454 (6)	23 (4)
O(6)	3381 (5)	901 (13)	1357 (6)	22 (4)
O(7)	2235 (6)	-2918 (11)	2412 (7)	22 (4)
C(1)	2189 (7)	-138 (20)	7251 (8)	18 (4)
C(2)	3772 (6)	607 (12)	7599 (8)	13 (4)
C(3)	4072 (6)	-213 (17)	5902 (7)	16 (4)
Na(1)	988 (3)	4518 (7)	3964 (4)	23 (2)
Na(2)	1347 (3)	4732 (8)	9515 (3)	21 (2)
H(C3)	385 (11)	-219 (25)	566 (13)	
H <sup>1</sup> (C3)	498 (11)	54 (26)	586 (12)	
H(C2)	453 (10)	-48 (24)	880 (12)	
H(O6)	404 (10)	-55 (25)	157 (13)	
H(O3)	336 (11)	414 (25)	767 (13)	

**Discussion.** Bond lengths and angles are given in Fig. 1. The carboxyl-group C—O lengths result from a resonance of C=O and C—O<sup>-</sup> and their lengths are in agreement with Evans (1976). The C—C bond lengths are well within the spread of reported values (Fenn & Marshall, 1972; Shefter & Trueblood, 1965). The C(2)—O(3) length is in agreement with those in other  $\alpha$ -hydroxy acids (Colton & Henn, 1965; Clark, 1964). The ester bond C(3)—O(4) is quite typical of many phosphate esters (Fewster, 1977), and the phosphate-group lengths are as expected (Watson & Kennard, 1973).

An intramolecular hydrogen bond occurs, O(3)—H(O3)···O(1), where H(O3)···O(1) is

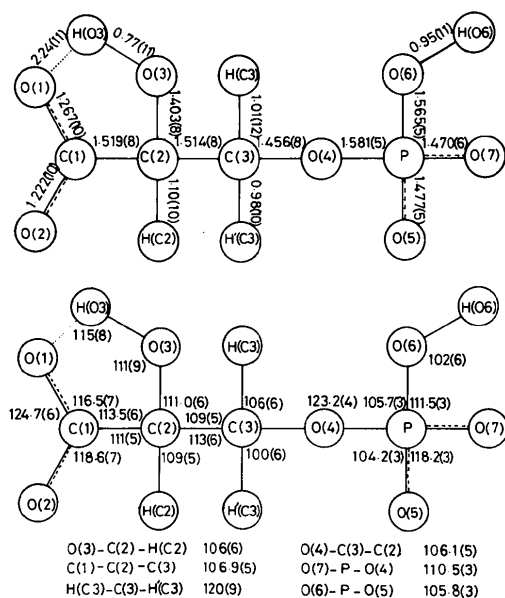


Fig. 1. Bond lengths (Å) and angles ( $^{\circ}$ ) for Na D-3-phosphoglycerate.

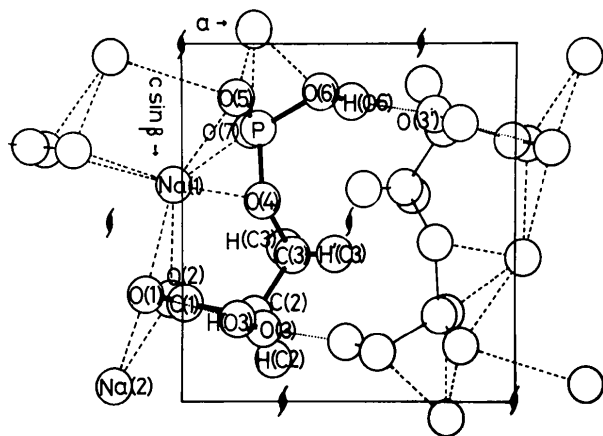


Fig. 2. Molecular configuration and packing showing the hydrogen bonding, and sodium cation contacts  $< 3 \text{ \AA}$ . O(2<sup>ii</sup>) is vertically above O(2).

Table 2. Distances (Å) from the best-fit plane

	Na salt	Cd salt
C(1)	0.0078 (8)	0.030 (3)
C(2)	0.0916 (8)	0.008 (3)
O(1)	0.0327 (6)	0.008 (3)
O(2)	0.0468 (9)	0.013 (2)
O(3)	0.0696 (7)	0.001 (2)
H(O3)	0.038 (13)	—

2.24 (11) Å and angle O(3)—H(O3)···O(1) is 115 (8) $^{\circ}$ . This bond is very weak (Chidambaram & Sikka, 1968), although it may account for the near-planar arrangement of atoms O(2), O(1), C(1), C(2) and O(3) (Fig. 2). H(O3) is also involved in the intermolecular H bond O(3)—H(O3)···O(1), where H(O3)···O(1) is 2.18 (11) Å and angle O(3)—H(O3)···O(2<sup>ii</sup>) is 161 (10) $^{\circ}$ . An intermolecular H bond also occurs, O(6)—H(O6)···O(3<sup>i</sup>), where H(O6)···O(3<sup>i</sup>) is 1.84 (9) Å and angle O(6)—H(O6)···O(3<sup>i</sup>) is 145 (10) $^{\circ}$ ; this is shown in Fig. 2, together with the coordination of the Na<sup>+</sup> cations.

The structure of cadmium D-3-phosphoglycerate trihydrate was determined by Mostad & Rosenqvist (1971), but, owing to the dominant scattering of the cation, e.s.d.'s are *ca* 3 $\times$  greater than in the present structure and H atoms could not be located.

The best-fit planes through atoms O(1), O(2), C(1), C(2) and O(3) for the two structures are given in Table 2. This group of atoms in the Cd salt is more closely planar than in the Na salt and H(O3) of the former is thought to be bonded to a water molecule and not involved in the shared contacts as in the latter. The bond lengths for both structures are within 2 e.s.d.'s of each other, except C(1)—O(1) in the carboxyl group which is 1.267 (10) Å in the Na salt and 1.34 (3) Å in the Cd salt, probably due to this O atom being coordinated to three Na<sup>+</sup> ions and a H atom in one case and to two Cd<sup>2+</sup> ions in the other. The bond angles differ slightly, the most significant difference being in the ester-link angle P—O(4)—C(3) which is 119 (1) $^{\circ}$  in the Cd salt and 123.2 (4) $^{\circ}$  in the Na salt. The phosphate groups in these two structures are in different orientations with respect to the remainder of the anion, and must therefore be free to rotate about the P—O(4) bond in solution.

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*Acta Cryst.* (1982). **B38**, 284–286

### 3,15-Dimethyl-18-(1-propynyl)-16-oxapentacyclo[10.4.2.0<sup>2,11</sup>.0<sup>3,8</sup>.0<sup>15,18</sup>]octadeca-4,7-dien-6-one

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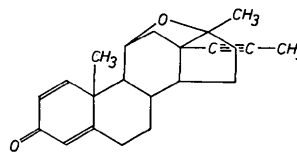
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(Received 19 February 1981; accepted 22 May 1981)

**Abstract.** C<sub>22</sub>H<sub>26</sub>O<sub>2</sub>, *M<sub>r</sub>* = 322.45, monoclinic, *P*2<sub>1</sub>, *Z* = 4, *a* = 20.383 (10), *b* = 7.316 (8), *c* = 12.094 (15) Å, β = 90.74 (6)°, *U* = 1803 (5) Å<sup>3</sup>, *D<sub>x</sub>* = 1.188, *D<sub>m</sub>* = 1.18 (2) Mg m<sup>-3</sup> by flotation in aqueous K<sub>2</sub>H<sub>9</sub>I<sub>4</sub>, μ(Mo *K*α) = 0.069 mm<sup>-1</sup>. The structure was solved, *via* the *h*0*l* projection, by direct methods and refined to *R* = 0.056 for 2902 unique diffractometer data [*F* > σ(*F*)]. The two virtually identical molecules in the asymmetric unit exhibit a steroid-like arrangement of three six- and one five-membered rings, with an additional transannular ether linkage.

**Introduction.** The title compound (I) was synthesized (at Roussel Uclaf, Romainville, France) according to a new rearrangement described by Teutsch, Lang, Smolik, Mornon & Delettré (1981). The crystals were of mediocre quality, so that out of the 4685 unique reflexions measured for 2θ < 56° with a Siemens computer-controlled diffractometer (Hoppe, 1965), Zr-filtered Mo *K*α radiation and crystal 0.75 × 0.25 × 0.2 mm only 2902 had *F* > σ(*F*). The crystal orientation and cell parameters were determined automatically by a 'systematically random' peak-search procedure described by Kobelt & Paulus (1979). After a number of fruitless attempts, the structure was solved by multiresolution tangent refinement, with several initial phases taken from a solution of the centrosymmetric

projection as recommended by Boeyens (1977). The structure was refined by least squares [2902 data, 433 parameters, *w* = 1/σ<sup>2</sup>(*F*)] to *R* = ∑Δ/∑*F<sub>o</sub>* = 0.056 and *R<sub>g</sub>* = [∑*w*Δ<sup>2</sup>/∑*wF<sub>o</sub>*<sup>2</sup>]<sup>1/2</sup> = 0.033. A riding model with idealized geometry (C–H 0.96 Å), and temperature factors fixed at 1.2 times the equivalent isotropic values for the C atoms to which they were attached, was employed for the H atoms; the remaining atoms were refined anisotropically. The ten largest peaks in a final difference electron density synthesis were between 0.14 and 0.17 e Å<sup>-3</sup>. Calculations were performed with a Nova 3/12 computer and the *SHELXTL* programs written by GMS.



**Discussion.** Coordinates and selected molecular dimensions are given in Tables 1–3.\* The two molecules in

\* Lists of structure factors, anisotropic temperature factors and hydrogen atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36193 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.