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Acta Cryst. (1976). B**32**, 488

The Crystal and Molecular Structure of Tetrasodium Carbonyldiphosphonate Dihydrate

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(*Received* 28 *February* 1975; *accepted* 23 *June* 1975)

The crystal and molecular structure of the dihydrated tetrasodium salt of carbonyldiphosphonate has been determined by single-crystal X-ray diffraction techniques using automated diffractometer-collected data and standard heavy-atom methods. $Na_4[OC(PO_3)_2].2H_2O$ (Na_4CDP) crystallizes in the noncentrosymmetric tetragonal space group $P\bar{4}$ with unit-cell dimensions $a=8{\cdot}489$ (1) and $c=6{\cdot}468$ (1) Å, and two formula units per unit cell. Full-matrix least-squares refinement resulted in both R_1 and $R_2=0{\cdot}037$ for 712 unique observed reflections. The crystal structure consists of carbonyldiphosphonate^{4-} ions bridged together primarily by coordination to sodium ions. The CDP^{4-} ion has (crystallographic) twofold symmetry with the PO_3 groups in an almost exactly staggered configuration. A comparison of this structure is made with the known structures of other diphosphonates. An examination of the interatomic bond lengths and angles indicates that any significant multiple P–C bonding is unlikely. Intramolecular electrostatic forces between the two negatively charged phosphonate groups appear to have marked effects on the structural features of the carbonyldiphosphonate molecule.

Introduction

Carbonyldiphosphonate, $OC(PO_3)_2^{4-}$ (CDP^{4-}), is one of a series of *gem*-diphosphonates which have been synthesized as part of a program directed at a study of metal chelating agents. The tetrasodium salt of carbonyldiphosphonate (Na_4CDP) was first prepared by Quimby, Prentice & Nicholson (1967) and in the course of characterization of this species unusual properties were revealed. The C–P bonds of carbonyldiphosphonate were found to be unusually resistant to hydrolytic cleavage; in mildly acidic solution the carbonyldiphosphonate molecule reversibly converts to a stable dihydroxymethylenediphosphonate. With respect to spectral properties an unusually low infrared carbonyl stretching frequency of 1612 cm^{-1} is observed; also, the yellow color of the material is due to an absorption maximum at 413 mμ (attributed to an $n\rightarrow\pi^*$ electronic transition of the carbonyl group), considerably lower in frequency than normally observed for ketones. Because of these unusual properties, as well as our continuing interest in metal chelation, for which this molecule has the potential *via* the two phosphonate groups and bridging carbonyl O atom, we deemed a single-crystal X-ray structural analysis of carbonyldiphosphonate to be important in the further characterization of this molecule. Reported here are the results of an analysis on the dihydrate of tetrasodium carbonyldiphosphonate, $Na_4CDP.2H_2O$.

Experimental

Single-crystal X-ray data collection

$Na_4CDP.2H_2O$ was obtained as well formed rod-shaped single crystals from Dr D. A. Nicholson of these laboratories. A single crystal of dimensions $0{\cdot}15\times0{\cdot}17\times0{\cdot}45$ (rotation (c) axis) mm was mounted with epoxy cement on a thin glass fiber. Preliminary oscillation, Weissenberg, and precession X-ray photographs indicated tetragonal $4/m$ symmetry. The crystal was optically aligned on a Siemens automated single-crystal diffractometer and 26 diffraction maxima were manually centered. Lattice constants were obtained (at 25°C) by least-squares refinement of the measured θ settings of these reflections. These lattice constants were used to generate diffractometer angle settings for all data reflections. The method of data collection closely paralleled a previously reported procedure (Uchtman & Gloss, 1972). 1564 reflections ($2\theta\leq60°$, Mo $K\alpha$ radiation) of which 42 had net intensities less than three times the standard deviation of the back-

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ground counts, were collected from the hkl, $\bar{h}\bar{k}l$, $\bar{h}kl$, and $h\bar{k}l$ octants. These reflections were later merged to a unique data set of 741 reflections, of which 712 were significantly above background. No extinction or absorption corrections were applied; the linear absorption coefficient (μ) is 6·99 cm^{-1} for Mo $K\alpha$ radiation and results in a μR max < 0·28. The relatively small values of the real and imaginary dispersion corrections for Mo $K\alpha$ radiation (*e.g.* $\Delta f' = 0{\cdot}1$ and $\Delta f'' = 0{\cdot}2$ for P) were assumed not to have a major effect on the crystal and therefore were neglected. The scattering factors used for all atoms were those compiled by Hanson, Herman, Lea & Skillman (1964).

Table 1. *Final atomic parameters for* $Na_4[OC(PO_3)_2].2H_2O$

Estimated standard deviations of last significant figures are given in parentheses.

	x	y	z
P	0·3313 (1)	−0·0913 (1)	0·2070 (2)
C	0·5	0·0	0·3502 (10)
O(1)	0·5	0·0	0·5454 (8)
O(2)	0·3879 (4)	−0·2624 (4)	0·1937 (5)
O(3)	0·1843 (4)	−0·0699 (5)	0·3366 (5)
O(4)	0·3242 (4)	−0·0110 (4)	−0·0035 (5)
O(5)	0·3201 (5)	0·3467 (5)	0·3423 (5)
H(1)	0·413 (8)	0·324 (8)	0·293 (9)
H(2)	0·311 (9)	0·355 (9)	0·461 (16)
Na(1)	0·0708 (2)	0·1813 (2)	0·2987 (3)
Na(2)	0·4614 (3)	0·2006 (3)	0·8620 (3)

Unit cell and space group

The lattice constants and their standard deviations for this crystal of $Na_4[OC(PO_3)_2].2H_2O$ are a = 8·489 (1) and c = 6·468 (1); the unit-cell volume is 466·1 Å^3. The experimental density of 2·21 ± 0·01 g cm^{-3} (determined by flotation in mixtures of dibromomethane and tetrachloroethylene) agrees well with the value of 2·24 for two formula units per unit cell. $F(000) = 312$. The lack of systematic absences indicated the possible space groups $P4$, $P4/m$ and $P\bar{4}$; from the size of the unit cell and expected molecular configuration $P\bar{4}$ (S_4^1, No. 81) was assumed to be the most likely space group. This assignment was verified by the successful refinement of the structure in this space group. The solution of the structure required the location of two Na, one P, one C, five O and two H atoms, corresponding to one-half the formula unit per unit cell. The crystallographically independent non-carbonyl group atoms were each found from the structural analysis to occupy the general fourfold set of positions: (x,y,z; $-x,-y,z$; $y,-x,-z$; $-y,x,-z$); the carbonyl group atoms were located on the special twofold set of positions: ($0,\frac{1}{2},z$; $\frac{1}{2},0,-z$).

Table 1 (*cont.*)

Hydrogen atoms were assigned an isotropic thermal parameter of 5·0 which was not varied in the course of the refinement. Anisotropic thermal parameters are of the form $\exp\,[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\times 10^{-5}]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	274 (15)	353 (16)	284 (21)	−440 (13)	−1 (20)	2 (19)
C	505 (93)	222 (82)	427 (142)	14 (67)	0	0
O(1)	1003 (91)	1028 (91)	311 (116)	−459 (71)	0	0
O(2)	519 (47)	489 (45)	1107 (83)	−6 (35)	−158 (63)	−145 (62)
O(3)	455 (45)	845 (55)	666 (77)	−13 (39)	111 (51)	−103 (56)
O(4)	822 (55)	759 (55)	471 (67)	−171 (45)	−171 (59)	289 (59)
O(5)	739 (58)	983 (63)	1009 (94)	208 (48)	−18 (61)	226 (65)
Na(1)	611 (29)	670 (30)	628 (40)	−74 (23)	−83 (36)	286 (36)
Na(2)	565 (31)	719 (34)	856 (48)	47 (24)	20 (33)	329 (35)

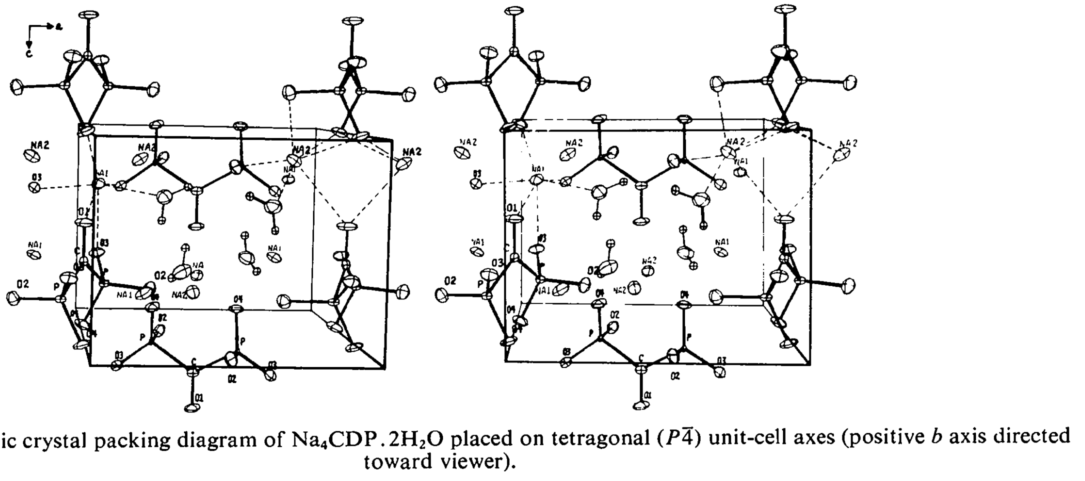

Fig. 1. Stereographic crystal packing diagram of $Na_4CDP.2H_2O$ placed on tetragonal ($P\bar{4}$) unit-cell axes (positive b axis directed toward viewer).

Determination of the structure

The X-RAY 67 system of computer programs (Stewart, 1967), modified for use on the Control Data Corp. 6600 computer, was used for the majority of computing operations. A statistical analysis of quasi-normalized structure factors (E's) (calculated using *DATFIX*) indicated our assumption of a non-centrosymmetric space group to be correct. In an ordered unit cell of space group $P\bar{4}$ the carbonyldiphosphonate group must be in such a position that the carbonyl group lies along a twofold rotation axis. A sharpened Patterson vector map revealed the positions of the atoms in the $OCPO_3$ fragment; an electron density map calculated using this fragment revealed the positions of the two Na ions and the O atom of the water molecule. Two cycles of full-matrix least-squares refinement using individual isotropic temperature factors, followed by three cycles using individual anisotropic ones, resulted in a discrepancy index of $R_1=[\sum||F_o|-|F_c||/\sum|F_o|]=0\cdot051$. Refinement was based on minimization of $\sum w_i\Delta F_i^2$, and weights were determined according to the relationships $w_i=1/\sigma_i^2(F_o)$, where $\sigma(F_o)$ was determined by counting statistics (see Stout & Jensen, 1968). A difference Fourier map calculated at this point revealed two likely positions for the water H atoms. These were included with isotropic temperature factors of 5·0 (which were not varied) in subsequent cycles of least-squares refinement. Final discrepancy indices are $R_1=0\cdot037$ and $R_2=[\sum w||F_o|-|F_c||^2/\sum w|F_o|^2]^{1/2}=0\cdot037$. In the last cycle of refinement all non-hydrogen positional parameter shifts were less than $0\cdot1\sigma$, where σ is the standard deviation of the parameter; the z parameters for H(2) shifted $\sim 1\sigma$ in the last cycle, while other H atom positional parameter shifts were $<0\cdot3\sigma$. A final difference Fourier map contained no peaks $>\sim|0\cdot5|$ e; any peaks with intensities $>|0\cdot3|$ e were sufficiently close to atom positions to be ascribable to uncorrected thermal motion. Final atomic positional and thermal parameters are listed in Table 1; Table 2 lists interatomic distances and angles.* The thermal ellipsoid plot program *ORTEP*

Table 2. *Interatomic distances* (Å) *and angles* (°) *for* $Na_4[OC(PO_3)_2].2H_2O$

Prime symbols indicate atom positions related to those in Table 1, as follows: $O(3)^{i}$ $(-x,-y,z)$; $O(3)^{ii}$, $O(2)^{ii}$ $(-y,x,1-z)$; $O(4)^{i}$ $(-y,x,-z)$; $O(1)^{i}$ $(y,1-x,1-z)$; $O(2)^{i}$, $O(4)^{iii}$ $(1-x,-y,1+z)$; $O(4)^{ii}$ $(x,y,1+z)$; $O(5)^{i}$ $(1-y,x,1-z)$; P^{i}, $O(1)^{ii}$, $O(2)^{iii}$ $(1-x,-y,z)$.

(*a*) Bond distances	
P——O(2)	1·533 (3)
P——O(3)	1·514 (4)
P——O(4)	1·524 (4)
P——C	1·874 (1)
C——O(1)	1·263 (7)
H(1)–O(5)	0·88 (7)
H(2)–O(5)	0·78 (10)
(*b*) Sodium coordination	
Na(1)···O(3)	2·353 (4)
Na(1)···$O(3)^{i}$	2·377 (4)
Na(1)···$O(3)^{ii}$	2·360 (4)
Na(1)···$O(4)^{i}$	2·319 (4)
Na(1)···$O(1)^{i}$	2·950 (3)
Na(1)···O(5)	2·556 (4)
Na(2)···$O(2)^{i}$	2·553 (4)
Na(2)···$O(2)^{ii}$	2·348 (4)
Na(2)···$O(4)^{ii}$	2·312 (4)
Na(2)···$O(4)^{iii}$	2·581 (4)
Na(2)···O(1)	2·684 (3)
Na(2)···$O(5)^{i}$	2·330 (4)
(*c*) Bond angles	
O(2)–P——O(3)	113·8 (2)
O(2)–P——O(4)	112·7 (2)
O(3)–P——O(4)	114·1 (2)
O(2)–P——C	100·4 (1)
O(3)–P——C	107·8 (1)
O(4)–P——C	106·7 (2)
P——C——P^{i}	120·7 (3)
P——C——$O(1)^{ii}$	119·6 (2)
H(1)–O(5)–H(2)	118·0 (7)
(*d*) Hydrogen-bond distances and angles	
O(5)···$O(2)^{iii}$	2·754 (5)
H(1)···$O(2)^{iii}$	1·88 (7)
O(1)···H(1)···$O(2)^{iii}$	176·0 (7)
H(2)···O(2)	2·29 (8)
[shortest intermolecular contact with H(2)]	
(*e*) Some nonbonding distances	
O(2)···O(3)	2·552 (5)
O(2)···O(4)	2·545 (5)
O(3)···O(4)	2·549 (5)
P······P^{i}	3·257
C···O(2)	2·626 (3)
C···O(3)	2·746 (3)
C···O(4)	2·733 (4)

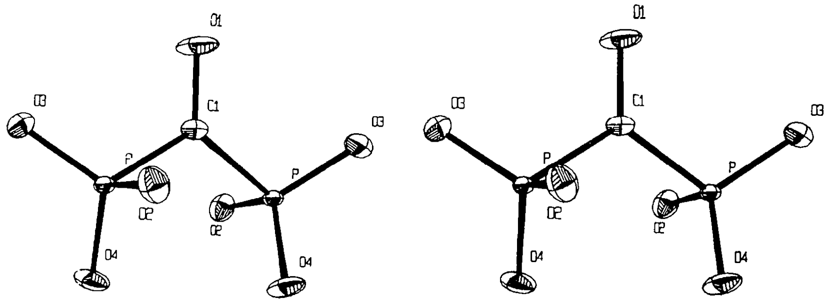

Fig. 2. Stereographic view of carbonyldiphosphonate anion.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31226 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

(C. K. Johnson, Oak Ridge National Laboratory) was used for crystal structure illustrations.

Results and discussion

The crystal structure of $Na_4CDP.2H_2O$ (Fig. 1) consists of carbonyldiphosphonate anions linked together in the crystal lattice almost entirely by coordination to Na^+ ions; the only apparent hydrogen bonding in the lattice is between the one crystallographically independent water molecule and one of the phosphonyl O atoms [O(5)···O(2), 2·754 (5) Å]. The two crystallographically independent Na ions are both six coordinate, each with distorted octahedral environments of four phosphonyl O atoms, one carbonyl O atom and one water molecule. The four phosphonyl O atoms coordinated to Na(1) are all at relatively short separations (range 2·319–2·377 Å) while the carbonyl O is at a rather long distance of 2·950 Å; the only chelation of a given CDP^{4-} to Na(1) involves the carbonyl O and a phosphonyl O [O(3)]. Na(2), on the other hand, is separated from four phosphonyl O atoms by distances ranging from 2·312 to 2·581 Å, and the carbonyl O is bound at a distance of 2·684 Å; the chelation between a given CDP^{4-} and Na(2) is tridentate involving two phosphonyl O atoms of one phosphonate group and one O of the other phosphonate group. The Na^+–carbonyl O binding for both Na^+ ions results in two ···ONaONaO··· chains zigzagging parallel to the *ab* plane and along the *a* axis (at $b=0$) in the case of Na(1) and the *b* axis (at $a=\frac{1}{2}$) in the case of Na(2).

The CDP^{4-} anion (Fig. 2) exists with C_2 (crystallographically imposed) symmetry; the twofold axis is coincident with the C–O bond. Bond distances and angles within the anion are not unusual; the P–O bond lengths (range 1·514–1·533 Å) are within the range of values expected for a fully ionized phosphonate or phosphate group. The O–P–C angles (average, 114°) are all slightly larger than the ideal tetrahedral value, while the O–P–O angles (average, 105°) are somewhat smaller; this is a situation similar to that found in $Na_4P_2O_7$ (Leung & Calvo, 1972) and other diphosphates. It is noteworthy (see below) that the O–P–O average value is somewhat larger and the O–P–C average value somewhat smaller than the corresponding values previously found in the structures of methylenediphosphonic acid (H_4MDP) (111°, 108°) (DeLaMatter, McCullough & Calvo, 1973), ethane-1-hydroxy-1,1-diphosphonic acid (H_4EHDP) (111°, 107°) (Uchtman & Gloss, 1972) and CaH_2EHDP (111°, 107°) (Uchtman, 1972). The two phosphonate groups have a nearly staggered configuration with respect to each other when viewed down the P···P axis (Fig. 3); one phosphonate group is rotated clockwise so that the torsion angle between the CPO(3)′ and PCP planes is +31·5°, while the other phosphonate group is rotated an equivalent amount in the opposite sense, *i.e.* −31·5° (in accord with the molecule's twofold symmetry). The two phosphonate groups are therefore staggered 63° with respect to each other. This relative arrangement of phosphonate groups is in contrast to that observed in two previously studied diphosphonic acids H_4MDP and H_4EHDP. In the former case the two groups are staggered only 35° with respect to each other so that the two CPO–PCP torsion angles are +23° and +58°; in the latter case the two groups are almost exactly eclipsed with torsion angles of ~0°. In the structures determined by Calvo and coworkers of several analogous pyrophosphates considerable variation has been observed in the relative orientations of PO_3 groups. The factors responsible for determining the relative configuration of PO_3 groups are undoubtedly subtle and have not yet to our knowledge been quantitatively elucidated. It was proposed in previous reports that steric effects of methylene substituents may play an important role in determining configurations of substituted methane diphosphonates; in the present case of CDP steric effects of the carbonyl O atom must be considerably less important. Of more importance here may be the minimization of repulsive interactions among negatively charged phosphonyl O atoms.

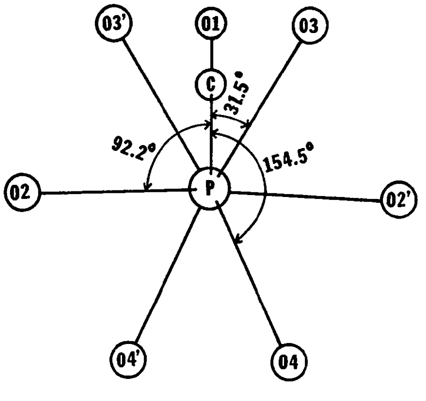
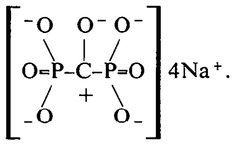


Fig. 3. Relative orientations of phosphonyl groups in CDP^{4-} viewed along PCP plane. Angles are indicated between OPC and PCP planes.

Of interest with respect to the aforementioned properties of CDP^{4-} are the parameters of the PC(O)P framework. The placement of atoms in this framework is quite close to that expected for bonding to an sp^2-hybridized C of a carbonyl group; the PCP and PCO angles are 120·7 and 119·6°, respectively, not statistically different from the ideal value of 120°. The P–C bond length of 1·874 Å compares with the average values of 1·792, 1·836 and 1·836 found for H_4MDP, H_4EHDP and CaH_2EHDP, respectively; the values found for these latter three diphosphonates are close to the mean value of 1·824 Å (68 determinations) for C(sp^3)–P(4-coordinate) single bonds (Naqvi, Wheatley & Foresti-Serantoni, 1971). The P–C bond in Na_4CDP is considerably longer than the value of 1·804 Å (118 determinations) found for C(sp^2)–P(4-

coordinate) bonds (Naqvi *et al.*, 1971). Long P–C bond lengths have also been reported for trisodium phosphonoformate (1·869 Å) (Naqvi *et al.*, 1971) and tetramethyl formadinium phosphonic anhydride (1·880 Å) (Sanz & Daly, 1972) and its parent acid (1·890 Å) (Daly, 1972). As was done by Naqvi *et al.* (1971) for phosphonoformate, we tend to attribute this lengthening of the P–C bond to repulsions between the negatively charged phosphonate groups. It is interesting to note that for the series of diphosphonates studied to date (H_4MDP, H_4EHDP, CaH_4EHDP and Na_4CDP), the trend in P–C bond lengths directly correlates with the extent and direction of distortion away from ideal tetrahedral angles about the P atoms. The length of the P–C bond in Na_4CDP, particularly when compared to the methylene and substituted methylene diphosphonates where only single P–C bonds are possible, suggests that multiple P–C binding (*e.g.* due to contribution of $p\pi$–$d\pi$ interaction) is not significant in this molecule.* The carbonyl distance of 1·263 Å is significantly longer than is normally found in ketones. This lengthening is consistent with the suggestion made by Quimby *et al.*, that CDP^{4-} may be stabilized by a significant contribution of a resonance form such as



$$\left[({}^{-}O)_2(O{=})P{-}\overset{O^{-}}{\underset{+}{C}}{-}P({=}O)(O^{-})_2\right]4Na^{+}.$$

Also consistent with this observation is the unusually low infrared carbonyl stretching frequency of 1612 cm^{-1}.

We would like to acknowledge the experimental assistance of R. A. Gloss and M. R. Webb, as well as helpful discussions with Dr B. H. Wiers.

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* This conclusion is also supported by the relative orientation of the carbonyl group and the PO_3 groups, since B. H. Wiers has shown (unpublished results) that $p\pi$–$d\pi$ orbital overlap is at a maximum when the molecule is in an eclipsed, planar 'W' (for an OPCPO chain of atoms) configuration. Also, Raman spectra results (W. Yellin, unpublished results) suggest an absence of coupling of the carbonyl frequencies with the symmetric PO_3 stretching mode.

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The Crystal and Molecular Structure of 5,5-Dimethyl-2-oxo-2-aminobenzo-1,3,2-dioxaphosphorinane

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(*Received* 11 *June* 1975; *accepted* 23 *June* 1975)

$C_{11}H_{16}NO_3P$, orthorhombic, $a=11·48$ (3), $b=11·37$ (3), $c=9·71$ (2) Å, space group $P2_12_12_1$, $Z=4$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations with 1200 independent reflexions to R 0·12. The dioxaphosphorinane ring has the chair configuration with the phosphoryl O atom, despite predictions to the contrary, in the equatorial position.

Introduction

In the chair form of 2-oxo-2-R-1,3,2-dioxaphosphorinanes the phosphoryl O atom can assume either an equatorial (I*a*) or an axial (I*b*) position. In most of the structures determined (Silver & Rudman, 1972; Drew & Rodgers, 1972; Wagner, Jensen & Wadsworth, 1973: and references therein) the O atom is equatorial though Galdecki & Karolak-Wojciechowska (1971) report a structure (II) where the O atom is axial. Mosbo & Verkade (1973) suggest from ^{1}H n.m.r. and dipole

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