

of 2.11 Å is somewhat smaller than the value of 2.16 Å found in the octahedral Ni(tren)(SCN)₂ (Rasmussen, 1959).

In the case of copper(II) trigonal bipyramidal stereochemistries have already been found by X-ray analysis (Mori, Saito & Watanabe, 1961; Bertrand, 1967; Kilbourn & Dunitz, 1967; Jain & Lingafelter, 1967).

For nickel(II), the structure of a low spin trigonal bipyramidal complex has been recently published (Stevenson & Dahl, 1967). Ni(Me₆tren)Br₂ is the only case of this type of configuration so far reported for a high spin nickel(II) complex.

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The structure of poly-L-proline II. By STRUTHER ARNOTT and S. DAVID DOVER, *Medical Research Council Biophysics Research Unit and Department of Biophysics, King's College, 26-29, Drury Lane, London, W. C.2, England*

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The crystal structure of poly-L-proline II (space group $P3_2$, $a=6.62$, $c=9.31$ Å (e.s.d.'s 0.01 Å) and three prolyl residues per unit cell) has been reappraised. Two crystal models have been considered: in the first the threefold helical molecules at each lattice point are all parallel; in the second there are two half coaxial antiparallel chains at each molecular site (such an arrangement corresponds to a statistical crystal structure in which each site is occupied, with equal probability, by up- and down-pointing chains). Refined molecular conformation and packing parameters have been obtained for both models by a least-squares method in which bond lengths and angles are constrained to have values in agreement with single-crystal analyses. The refined *non-statistical* model (with standard conformational angles $\varphi=99.8^\circ$, $\psi=-95.1^\circ$, $\omega=-0.4^\circ$) provides a markedly better fit with the X-ray intensities and is preferred also on stereochemical grounds.

Cowan & McGavin (1955) analysed the X-ray diffraction from doubly oriented films of poly-L-proline II and found a trigonal unit cell, space group $P3_2$, with $a=6.62$, $c=9.36$ Å (we find $a=6.62$, $c=9.31$ Å both with e.s.d. 0.01 Å). They concluded also that the three prolyl residues in each unit cell were in a single molecule related by the same left-handed screw triad as the space group. Sasisekharan (1959) published a similar molecular model and from consideration of intermolecular contacts and optical transforms decided the radius vector of one αC made an angle, ψ , between 30° and 35° , with \mathbf{a} . Burge, Harrison & McGavin (1962) determined ψ to be $40 \pm 2^\circ$ by examining the variation of R with ψ . A feature of both crystal models is a short (2.80 Å) $\gamma C \cdots O$ contact between molecules which might be a $CH \cdots O$ hydrogen bond.

We have refined the crystal structure of poly-L-proline II using powder diffraction data and the linked-atom method of Arnott & Wonacott (1966a). In this method bond lengths and angles can be kept fixed at standard values while the variables are the chain dihedral angles (τ), the radius of αC (D) and the Eulerian angles ($\theta_x, \theta_y, \theta_z$) which determine the chain orientation. Additional parameters are the scale (K), the average isotropic temperature factor (B) and the molecular orientation (ψ). By those means the number and kind of variables is rendered appropriate to the paucity (only fifteen in this case) and low resolving power of intensity data given by the polymer.

The function minimized in a least-squares fashion was

$$\Theta = \Phi + \sum_h \lambda_h G_h \quad (1)$$

where

$$\Phi = \sum_m \omega_m \{ \sigma F_m - (1/K) c F_m \exp(-BQ^2/4) \}^2 \quad (2)$$

and λ_h is the Lagrange multiplier appropriate to the constraint, $G_h=0$ to be imposed on the solution. Six equations, $G_h=0$, involving some of the cylindrical polar atomic coordinates with

$$\begin{aligned} G_1 &= R(1) - R(7), & G_2 &= \varphi(1) - \varphi(7) + 120^\circ, \\ G_3 &= Z(1) - Z(7) - c/3, & G_4 &= R(4) - R(7a), \\ G_5 &= Z(4) - Z(7a) - c/3, & G_6 &= Z(5) - Z(8) - c/3, \end{aligned}$$

were used so that all prolyl residues were joined appropriately in a left-handed threefold helix of pitch equal to c . (The atom numbering key is in Fig. 1.)

We have also considered another possible crystal model to determine if poly-L-proline has a statistical crystal structure like other polypeptides such as α -poly-L-alanine (Elliott & Malcolm, 1959; Arnott & Wonacott, 1966b) and β -poly-L-alanine (Arnott, Dover & Elliott, 1967). The second model has two half (coaxial) molecules at each lattice point, the half molecules having $-\text{CO.NH.CH=}$ sequences of opposite sense. For such a model two more parameters are

needed: the relative translation (TRANS) and relative orientation (ROT) of, say, the up-pointing half molecule with respect to the down-pointing one.

The same standard bond lengths and angles (see Fig. 1) were used in both cases. Although the statistical model has more degrees of freedom ($12-6=6$) than the model with parallel chains ($10-6=4$), a significantly better fit to the observed data was obtained with the latter, which had minimum $\Phi=1.1 \times 10^5$ and $R=0.077$ against $\Phi=2.9 \times 10^5$, $R=0.134$. (Observed and calculated structure amplitudes are in Table 1.) The parameters and atomic coordinates of the two refined models are listed in Tables 2 and 3, where it can be seen that the non-statistical model has also the more credible temperature factor. The non-statistical model is further favoured by stereochemical considerations: $\tau_{67}=180.4^\circ$ shows that the expected coplanarity of the atoms about the peptide bond has scarcely been violated in the refinement, but the value 176.5° for the alternative model is less satisfactory; the statistical model has an unacceptably short intermolecular $\gamma\text{C}\cdots\gamma\text{C}$ contact of 2.8 \AA , while in the non-statistical model the only such short contact is the $\gamma\text{C}\cdots\text{O}$ distance of 2.80 \AA noted previously. The possibility of a $\text{CH}\cdots\text{O}$ intermolecular interaction occurring between poly-L-proline helices therefore appears to have a sound experimental basis. We have, however, no evidence that there is an attractive force between these atoms. Since other orientations of the awkwardly shaped poly-L-proline II molecule lead to more serious short contacts it is more likely that the situation we observe is merely the best compromise. It is of interest also, that of the two possible puckers of the pyrrolidine ring that Leung & Marsh (1958) found equally likely in L-leucyl-L-prolylglycine, only one (the C_6 of Leung & Marsh) is probable in polyproline since the alternative results in a $\gamma\text{C}\cdots\text{O}$ distance of only 2.6 \AA .

Table 1. Observed and calculated structure amplitudes for the two models for poly-L-proline II

The scale is arbitrary and non-accidentally overlapping reflexions (hkl , khl etc) are listed together under one set of indices (hkl).

h	k	l	F_o	F_c (Non-statistical)	F_c (Statistical)
1	0	0	127	125	135
1	0	1	155	146	138
1	0	2	112	120	126
1	1	0	23	40	51
1	1	1	94	93	98
0	0	3			
2	0	0			
2	0	1	141	150	129
1	0	3			
1	1	2			
2	0	2	88	93	73
1	1	3	66	54	59
2	1	0	62	65	54
1	0	4			
2	1	1			
2	0	3	64	55	84
2	1	2			
2	1	2	98	79	83
3	0	0	82	84	83
1	1	4			
3	0	1			
2	0	4			
2	1	3	51	51	62
1	0	5			
3	0	2	88	89	93

The only short non-bonded, intramolecular interatomic distance (apart from those associated with the planarity of the peptide group) is 2.8 \AA between N and O of successive residues. This is within 0.2 \AA of the sum of standard van der Waals radii and therefore allowable.

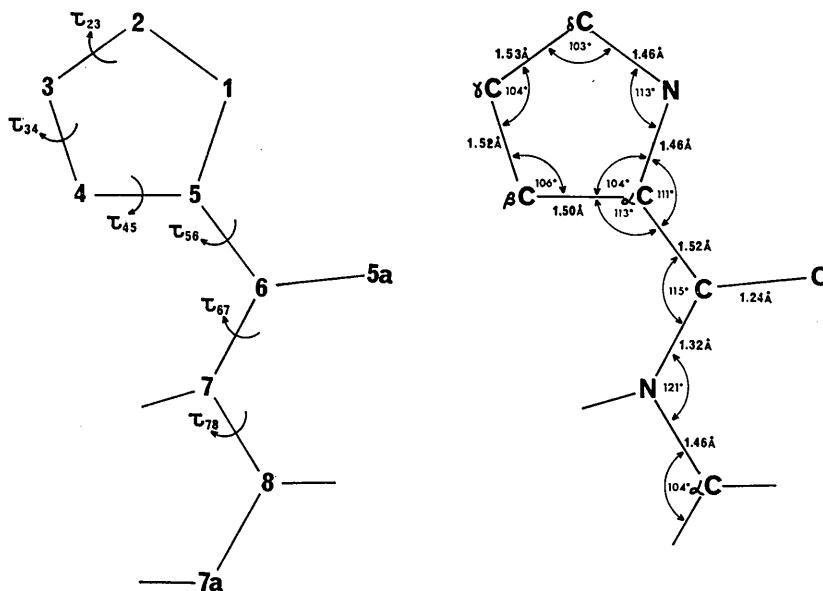


Fig. 1. Left: the atomic numbering and conformational parameters of poly-L-proline. During the refinements the pyrrolidine ring parameters (τ_{23} , τ_{34} , τ_{45}) were kept constant. Right: the stereochemistry used in the two linked atom refinements of poly-L-proline II structures.

Table 2. *The crystal and molecular parameters of the two refined poly-L-proline II models*

	The angles in italics were not refined.	
	Non-statistical	Statistical
τ_{23}	<i>-23.8°</i>	<i>-23.8°</i>
τ_{34}	<i>31.4</i>	<i>31.4</i>
τ_{45}	<i>94.7</i>	<i>94.7</i>
τ_{56}	95.1	96.5
τ_{67}	180.4	176.5
τ_{78}	200.2	201.8
θ_x	1.0	-1.8
θ_y	232.4	231.2
θ_z	55.2	54.5
D	1.244 Å	1.243 Å
ψ	42.4°	10.7°
ROT	-	-65°
TRANS	-	-6.923 Å
K	2.400	2.413
B	5.10 Å ²	0.832 Å ²

The refined crystal structure we prefer is very similar to that of Burge *et al.* (1962), and has standard (*J. Mol. Biol.* (1966), **15**, 399) polypeptide chain parameters $\varphi = 99.8^\circ$, $\psi = -95.1^\circ$, $\omega = -0.4^\circ$.

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The crystal structure of Zr₂Se* By H.F. FRANZEN and L.J. NORRBY†, *Institute for Atomic Research and Department of Chemistry Iowa State University, Ames, Iowa, U.S.A.*

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The crystal structure of Zr₂Se has been determined and refined by X-ray single-crystal methods. Zr₂Se was found to be isostructural with Ta₂P [Nylund, *Acta Chem. Scand.* (1966), **20**, 2393] and with Ti₂S [Owens, Conard & Franzen, *Acta Cryst.* (1967), **23**, 77].

The coordination polyhedra types between trigonal prismatic and tetrakaidecahedral found for boron, silicon and phosphorus in many compounds of these elements with transition elements (Aronsson, Lundström & Rundqvist, 1965) were recently found also for sulphur in Ti₂S (Owens, Conard & Franzen, 1967) and in Nb₂S₈ (Franzen, Beineke & Conard, 1968). The work reported here was carried out with the purpose of further exploring the crystal chemistry of the lower chalcogenides of transition elements, and in particular to determine whether other cases of augmented trigonal prismatic coordination could be found for chalcogens.

The method of high temperature preparation has been described previously (Owens, Conard & Franzen, 1967). In the case of Zr₂Se the sample was prepared at a final annealing temperature of 1550°C. The single-crystal X-ray diffraction data were collected with a Hilger-Watts full circle diffractometer coupled to an SDS-910 computer in

Table 3. *The cylindrical polar coordinates of the basic (up) poly-L-proline chain unit*

	Non-statistical			Statistical		
	R (Å)	φ (°)	Z (Å)	R (Å)	φ (°)	Z (Å)
$\alpha C(3)$	1.24	0	0	1.24	0	0
$C(1)$	0.27	12.0	1.16	0.32	14.7	1.20
$N(1)$	1.04	-75.3	1.95	1.03	-73.9	1.97
$O(1)$	1.14	114.6	1.34	1.15	109.2	1.41
$\alpha C(1)$	1.24	-120.0	3.10	1.24	-120.0	3.10
$\beta C(1)$	2.64	-105.2	3.40	2.65	-106.1	3.35
$\gamma C(1)$	3.19	-79.2	2.86	3.21	-80.2	2.82
$\delta C(1)$	2.45	-67.3	1.66	2.44	-67.4	1.65

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a configuration described elsewhere (Dahm, Benson, Nimrod, Fitzwater & Jacobsen, 1967). Mo $K\alpha$ radiation was used with balanced Zr and Y filters to collect data for about 1300 reflections at $2\theta \leq 80^\circ$.

The Lorentz, polarization and absorption corrections were applied as described previously (Franzen, Beineke & Conard, 1968). The standard deviations of all observations were obtained with the use of the law of propagation of errors and estimated standard deviations in the θ angle and the absorption factor and standard deviations in the intensities (corrected for background) based on counter statistics. Data were accepted only if $\sigma(I)/I < 0.4$, leaving 438 independent reflections.

The lattice parameters were determined from a Guinier powder photograph at 25°C using KCl as internal standard and Cu $K\alpha_1$ radiation, $\lambda = 1.54050 \text{ \AA}$:

$$a = 12.6400 \pm 27 \text{ \AA}, \quad b = 15.7968 \pm 32 \text{ \AA}, \quad c = 3.6016 \pm 10 \text{ \AA}, \\ V = 719.1 \pm 3 \text{ \AA}^3.$$

With $Z = 12$, (*cf.* below), $D_x = 7.24 \text{ g.cm}^{-3}$.

By comparison of the Weissenberg pattern of Zr₂Se with that of Ti₂S it seemed likely that these two compounds are isostructural. Accordingly the Ti₂S positions were used as

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