Structure of *cyclo*(-L-Pro-L-Pro-Gly-L-Pro-L-Leu-Gly-) Methanol Solvate Monohydrate, C₂₅H₃₈N₆O₆.CH₃OH.H₂O

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Abstract. $M_r = 568.6$, orthorhombic, $P2_12_12_1$, $a = 11.635$ (2), $b = 17.716$ (3), $c = 14.334$ (1) Å, $Z = 4$, $V = 2954.0$ (7) Å^3, $D_x = 1.278$, $D_m = 1.28$ g cm^{-3}, $\lambda(\text{Cu }K\alpha) = 1.5406$ Å, $\mu(\text{Cu }K\alpha) = 8.0$ cm^{-1}, $F(000) = 932$, room temperature. $R = 0.077$ for 2439 observed reflections. The molecular structure is characterized by a type-I β turn with Pro-Leu at the corner in a half of the molecule and two consecutive *cis* peptide bonds, Gly-Pro and Pro-Pro, in the other half. One of the *cis* peptide bonds is severely distorted from planarity with $\omega = -17.3°$.

Introduction. The structure and chemistry of many cyclic oligopeptides, including both synthetic and naturally occurring peptides, have been studied to clarify the mechanisms of biological activity of the naturally occurring cyclic oligopeptides, *e.g.* antamanide (Karle, Wieland, Schermer & Ottenheym, 1979). As part of these studies, a cyclic hexapeptide, *cyclo*(-Pro¹-Pro²-Gly³-Pro⁴-Leu⁵-Gly⁶-) (hereafter PPGPLG), was synthesized and the crystal structure studied by X-ray diffraction. It is known by the X-ray studies that many linear oligopeptides having the Pro-Leu sequence prefer to form a type-I β turn (Ashida, Yamane & Tanaka, 1980), and also the proline residue rarely occupies the third position of the β turn. Therefore PPGPLG is expected to form a β turn only at the Pro-Leu part.

Experimental. The linear hexapeptide, Boc-Pro-Pro-Gly-Pro-Leu-Gly-OSu (Boc: *tert*-butoxycarbonyl; OSu: *N*-hydroxysuccinimide ester), prepared by the DCC (dicyclohexylcarbodiimide) coupling method in the liquid phase was added to pyridine to yield the title compound (Kuromizu & Izumiya, 1970). It was purified by gel permeation chromatography. Rather large colorless block crystals were obtained from a methanol solution. The identification of the compound was made by FD mass spectroscopy by courtesy of Drs Y. Shimonishi and S. Aimoto of the Institute for Protein Research in Osaka University.

Crystal $0.4 \times 0.3 \times 0.3$ mm, D_m measured by flotation in CCl₄/*n*-hexane; cell dimensions measured on the diffractometer by least-squares refinement of 14

selected reflections in the interval $0.184 < \sin\theta/\lambda < 0.325$ Å^{-1}; data collected on a Rigaku four-circle diffractometer, graphite-monochromatized Cu $K\alpha$ radiation, ω–2θ scan mode; Lorentz–polarization corrections but not absorption; 2439 independent reflections collected, 2007 non-zero reflections with $|F_o| > 3\sigma_F$ in the range $\sin\theta/\lambda < 0.583$ Å^{-1} used for the structure determination, no equivalent reflections measured; intensities of three standard reflections (200, 060, 004) monitored every 100 reflections showed no significant reduction; structure solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), all the main-chain atoms and a part of the side-chain atoms from an E map; refinement by block-diagonal least-squares program *HBLS* VI (Ashida, 1981) with anisotropic thermal parameters for all the non-H atoms and with isotropic ones for the H atoms (located geometrically); thermal parameters of H atoms not refined; $\sum w||F_o| - |F_c||^2$ minimized, $R = 0.077$ for all reflections (0.070 for non-zero reflections), $R_w = (\sum w||F_o|^2 - |F_c|^2|/\sum w|F_o|^2)^{1/2} = 0.079$, $w = 0.17$ for $F_o = 0.0$, $w = 1/[\sigma(F_o) + 0.028|F_o| + 0.00054|F_o|^2]$ for $F_o > 0.0$, $S = 1.43$; $(\Delta/\sigma)_{\max}$ in final refinement $= 0.95$, $(\Delta/\sigma)_{\text{ave}} = 0.33$, final maximum $\Delta\rho$ height 0.18, minimum -0.38 e Å^{-3}; scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Fig. 1 shows the atomic numbering. The atomic coordinates of the non-H atoms are listed in Table 1 and the bond lengths, angles and torsion angles are shown in Tables 2, 3 and 4.* The thermal vibrations of all C$^\gamma$ of Pro and C$^\gamma$ and C$^\delta$ of Leu⁵ are unusually large. These large thermal vibrations cause the neighboring bond lengths and angles to be unusual, *e.g.* the bond length of C$^\gamma$–C$^{\delta_2}$ of Leu⁵ is extraordinarily short. This may indicate the possibility of the co-existence of different conformations of the side chains.

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* Lists of structure factors, anisotropic thermal parameters, and atomic coordinates of H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38894 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional* ($\times 10^4$) *and thermal* ($\times 10$) *parameters of non-hydrogen atoms with standard deviations*

$B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$ (Hamilton, 1959).

	x	y	z	$B_{eq}(\text{Å}^2)$
C(1α)	997 (5)	4379 (3)	92 (4)	41 (3)
C(1β)	265 (6)	4277 (4)	981 (5)	62 (4)
C(1γ)	−729 (7)	4784 (5)	895 (6)	80 (5)
C(1δ)	−749 (5)	5084 (4)	−84 (5)	54 (3)
C(1)	968 (5)	3663 (3)	−494 (4)	42 (2)
C(2α)	2417 (5)	3067 (3)	563 (4)	42 (3)
C(2β)	2811 (8)	2252 (4)	609 (6)	77 (5)
C(2γ)	2203 (14)	1845 (7)	−79 (11)	173 (12)
C(2δ)	1545 (7)	2352 (4)	−696 (6)	63 (4)
C(2)	3421 (5)	3618 (3)	390 (4)	41 (3)
C(3α)	4837 (5)	4415 (5)	1153 (4)	41 (2)
C(3)	4340 (5)	5206 (3)	1164 (4)	36 (2)
C(4α)	4664 (5)	6543 (3)	1454 (4)	40 (3)
C(4β)	5729 (7)	6983 (4)	1775 (5)	62 (4)
C(4γ)	6677 (8)	6515 (6)	1579 (8)	103 (6)
C(4δ)	6308 (5)	5695 (4)	1560 (5)	56 (3)
C(4)	4118 (5)	6893 (3)	605 (4)	37 (2)
C(5α)	3923 (5)	6917 (3)	−1089 (4)	37 (2)
C(5β)	4841 (6)	7175 (4)	−1794 (5)	52 (3)
C(5γ)	5379 (8)	7971 (6)	−1573 (5)	99 (6)
C(5δ1)	6231 (9)	8122 (7)	−2363 (7)	116 (7)
C(5δ2)	5712 (11)	8194 (6)	−729 (9)	122 (8)
C(5)	3078 (5)	6362 (3)	−1527 (4)	40 (2)
C(6α)	2065 (5)	5151 (3)	−1456 (4)	41 (3)
C(6)	823 (5)	5290 (3)	−1198 (4)	42 (3)
C(M)*	5870 (9)	4933 (5)	−1464 (6)	83 (5)
N(1)	435 (4)	4983 (2)	−403 (3)	39 (2)
N(2)	1609 (4)	3073 (3)	−214 (3)	40 (2)
N(3)	3945 (4)	3847 (3)	1173 (3)	39 (2)
N(4)	5075 (4)	5771 (3)	1327 (3)	38 (2)
N(5)	4411 (4)	6623 (2)	−235 (3)	34 (2)
N(6)	2814 (4)	5734 (2)	−1072 (3)	36 (2)
O(1)	363 (4)	3629 (3)	−1196 (3)	55 (2)
O(2)	3749 (4)	3782 (3)	−388 (3)	53 (2)
O(3)	3321 (3)	5326 (2)	1010 (3)	42 (2)
O(4)	3449 (4)	7422 (2)	701 (3)	54 (2)
O(5)	2668 (4)	6522 (2)	−2307 (3)	55 (2)
O(6)	216 (4)	5711 (3)	−1679 (3)	57 (2)
O(M)*	6232 (4)	5515 (3)	−817 (3)	67 (3)
O(W)*	−2028 (4)	6285 (3)	−1739 (4)	66 (2)

* *M* and *W* indicate methanol and water respectively.

Table 2. *Bond lengths* (Å) *with standard deviations*

	Pro¹	Pro²	Gly³	Pro⁴	Leu⁵	Gly⁶
N(i)—C(iα)	1·442 (7)	1·459 (8)	1·446 (8)	1·460 (7)	1·446 (7)	1·457 (7)
C(iα)—C(i)	1·552 (8)	1·542 (8)	1·516 (8)	1·507 (8)	1·525 (8)	1·513 (8)
C(i)—O(i)	1·229 (7)	1·215 (7)	1·225 (7)	1·225 (7)	1·246 (8)	1·238 (7)
C(i)—N(i+1)	1·346 (7)	1·339 (7)	1·338 (7)	1·341 (7)	1·328 (7)	1·341 (7)
C(iα)—C(iβ)	1·543 (10)	1·517 (11)		1·533 (10)	1·539 (9)	
C(iβ)—C(iγ)	1·471 (12)	1·410 (18)		1·409 (14)	1·573 (13)	
C(iγ)—C(iδ)	1·503 (12)	1·473 (18)		1·514 (14)		
C(iδ)—N(i)	1·464 (8)	1·455 (9)		1·479 (9)		
C(iγ)—C(iδ1)					1·331 (17)	
C(iγ)—C(iδ2)					1·528 (17)	

Table 4. *Conformational angles* (°) *with standard deviations*

	Pro¹	Pro²	Gly³	Pro⁴	Leu⁵	Gly⁶
φ	−65·9 (7)	−63·7 (7)	84·5 (6)	−63·6 (7)	−107·7 (6)	−90·5 (6)
ψ	169·6 (4)	157·0 (4)	167·5 (4)	−24·2 (8)	5·4 (7)	−89·8 (6)
ω	−5·6 (9)	−174·4 (4)	−173·3 (4)	179·3 (4)	−176·5 (4)	−17·3 (8)
χ^1	5·0 (8)	2·6 (10)		14·7 (8)		
χ^2	10·3 (9)	9·0 (15)			−78·6 (7)	
χ^{21}					44·0 (14)	
χ^{22}					−178·3 (6)	
χ^3	−21·4 (8)	−11·5 (13)		24·8 (10)		
χ^4	35·7 (7)	9·8 (9)		−14·7 (8)		
θ	−19·4 (7)	−4·8 (7)		0·9 (7)		

Codes: $\varphi = C(i-1)-N(i)-C(i\alpha)-C(i)$; $\psi = N(i)-C(i\alpha)-C(i)-N(i+1)$; $\omega = C(i\alpha)-C(i)-N(i+1)-C(i+1\alpha)$; $\chi^1 = N(i)-C(i\alpha)-C(i\beta)-C(i\gamma)$; $\chi^2 = C(i\alpha)-C(i\beta)-C(i\gamma)-C(i\delta)$; $\chi^{21} = C(i\alpha)-C(i\beta)-C(i\gamma)-C(i\delta1)$; $\chi^{22} = C(i\alpha)-C(i\beta)-C(i\gamma)-C(i\delta2)$; $\chi^3 = C(i\beta)-C(i\gamma)-C(i\delta)-N(i)$; $\chi^4 = C(i\gamma)-C(i\delta)-N(i)-C(i\alpha)$; $\theta = C(i\delta)-N(i)-C(i\alpha)-C(i\beta)$.
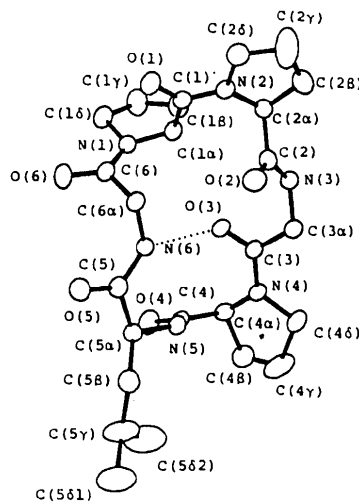
Fig. 1. Molecule with the numbering scheme and 30% probability plots for thermal ellipsoids. Dotted line indicates the 4→1 intramolecular hydrogen bond.

Table 3. *Bond angles* (°) *with standard deviations*

	Pro¹	Pro²	Gly³	Pro⁴	Leu⁵	Gly⁶
C(i−1)—N(i)—C(iα)	124·6 (5)	126·3 (5)	121·3 (5)	121·0 (5)	122·2 (4)	123·1 (5)
N(i)—C(iα)—C(i)	109·6 (5)	111·1 (5)	111·7 (5)	115·0 (5)	111·8 (4)	111·3 (6)
C(iα)—C(i)·O(i)	120·6 (5)	122·5 (5)	121·8 (5)	119·5 (5)	118·1 (5)	120·5 (5)
C(iα)—C(i)—N(i+1)	117·9 (5)	113·6 (5)	116·8 (5)	118·1 (5)	119·1 (5)	117·6 (5)
O(i)—C(i)—N(i+1)	121·5 (5)	123·8 (6)	121·4 (5)	122·4 (5)	122·9 (5)	121·8 (5)
N(i)—C(iα)—C(iβ)	104·1 (5)	103·5 (5)		104·5 (5)	113·0 (5)	
C(iβ)—C(iα)—C(i)	110·3 (5)	112·4 (6)		112·0 (5)	111·6 (5)	
C(iα)—C(iβ)—C(iγ)	107·1 (6)	107·8 (9)		105·9 (7)	114·2 (6)	
C(iβ)—C(iγ)—C(iδ)	107·8 (7)	111·7 (11)		110·3 (9)		
C(iγ)—C(iδ)—N(i)	103·5 (6)	102·9 (8)		101·1 (7)		
C(iδ)—N(i)—C(iα)	111·4 (5)	112·9 (5)		112·0 (5)		
C(iδ)—N(i)—C(i−1)	122·2 (5)	120·9 (5)		126·3 (5)		
C(iβ)—C(iγ)—C(iδ1)					124·5 (10)	
C(iβ)—C(iγ)—C(iδ2)					105·6 (9)	
C(iδ1)—C(iγ)—C(iδ2)					115·8 (11)	

The molecular structure is characterized by a β turn in a half of the molecule and two *cis* peptide bonds in the other half. None of the hydrophilic atoms with the exception of O(3) and N(6) point toward the center of the molecule. Therefore this molecule would seem to lack the ability to act as an ionophore if no severe deformation is possible.

PPGPLG has three pyrrolidine rings, Pro[1], Pro[2] and Pro[4]. In general, the pyrrolidine ring is puckered and the conformations are classified as of either C_s or C_2 symmetry (Ashida & Kakudo, 1974). In Pro[4], the ring shows approximate C_s symmetry with the symmetry element passing through C^γ, the ring conformations being classified as C_s-C^γ-*endo*.

The pyrrolidine ring of Pro[2] is roughly planar because of the small deviations of C^β and C^γ from the plane of N, C^α and C^δ. This planarity attributes to the large thermal vibration ($B_{eq} = 17.3$ Å^2) of C^γ. In the course of the refinement of the structure, a structural model having two sites for C^γ on either side of the plane, with one-half occupancy for each, showed no definite improvement. A remarkable puckering occurs in Pro[1], *i.e.* both C^β and C^γ deviate from the plane of N, C^α and C^δ in the same direction. This is a unique conformation for a pyrrolidine ring.

The type-I β turn occurs at Gly[3]-Pro[4]-Leu[5]-Gly[6] as expected, the intramolecular hydrogen bond being N(6)—H$\cdots$O(3). Although its length of 3.13 Å is definitely longer than most of the intermolecular N—H$\cdots$O hydrogen bonds, such a long hydrogen bond is not unusual in a β turn. The torsion angles and the hydrogen-bond lengths in the β turn are not different from those of β turns having the same Pro-Leu sequences.

The other half of the molecule is characterized by two consecutive *cis* peptide bonds of Gly[6]-Pro[1] and Pro[1]-Pro[2]. The peptide plane between Gly[6] and Pro[1] is considerably distorted, $\omega = -17.3°$. This distortion seems to be caused by the demands of such a small ring formation of six residues.

Though the peptide bond between the common amino acid residues is more stable in the *trans* form than in the *cis* form, the N-substituted peptide bonds made by proline are sometimes folded in the *cis* form, especially in cyclic oligopeptides. In linear oligopeptides, the only example of a *cis*-peptide bond reported is in Z-Gly-Pro-Leu (Yamane & Ashida, 1976). According to the studies by Zimmerman & Scheraga (1976), the energy difference between the *trans* and *cis* forms is reduced from 34 kJ mol^{-1} in the unsubstituted peptide bond to 4 ~ 8 kJ mol^{-1} in the N-substituted one. But the occurrence in PPGPLG of two successive *cis* peptide bonds is a rare case, except for the *cis* peptide bonds in *cyclo*(-tri-Pro-) (Druyan, Coulter, Walter, Kartha & Ambady, 1974) and póly-Pro(I) (Traub & Shmueli, 1963).

The crystal packing scheme is shown in Fig. 2. The hydrogen bonds are summarized in Table 5. There are six intermolecular hydrogen bonds which connect peptides and the solvent molecules. A short C—H$\cdots$O contact between C^α of Pro[2] and O=C of Leu[5] is deemed a hydrogen bond because of the structural geometry. Such a short C—H$\cdots$O hydrogen bond is also found in the crystal structure of Boc-Val-Pro-Gly-Gly-OBzl in which C^α of Gly plays the role of donor (Ayato, Tanaka & Ashida, 1981).

Recently the crystal structure of *cyclo*(-Pro-Pro-Gly-Pro-Pro-Gly-) (hereafter PPGPPG), in which the main-chain skeleton is very similar to that of PPGPLG, has been reported (Czugler, Sasvári & Hollósi, 1982). This compound forms a type-I β turn at Gly-Pro-Pro-Gly, the first example of a type-I β turn having Pro at the third site, and two consecutive *cis* peptide bonds on the other side.

A comparison of the conformational angles shows that the main chain of PPGPPG has fewer distortions than that of PPGPLG although the β turn in PPGPPG has a proline residue in the third position. PPGPLG shows a severe distortion of the *cis* peptide plane between Gly[6] and Pro[1]. The planarity of the corresponding peptide bond of PPGPPG is not so unusual, $\omega = 8.0°$.
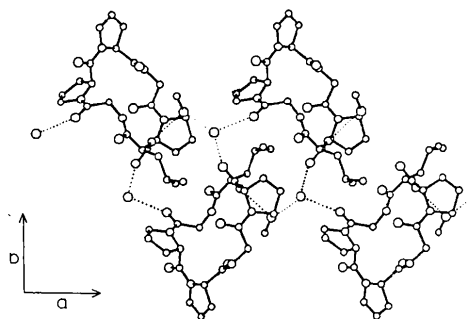
Fig. 2. Crystal packing viewed down the *c* axis. Hydrogen bonds are indicated by dotted lines.

Table 5. *Hydrogen-bond distances and angles*

D	A	H$\cdots$A (Å)	D$\cdots$A (Å)	∠D—H$\cdots$A (°)
N(6)$\cdots$O(3^i)		2.26 (6)	3.128 (6)	164 (5)
N(5)$\cdots$O(M^i)		2.21 (6)	3.007 (7)	159 (6)
N(3)$\cdots$O(5^{ii})		2.12 (6)	2.948 (7)	160 (6)
O(W)$\cdots$O(6^i)		1.88 (8)	2.804 (7)	160 (7)
O(M)$\cdots$O(W^{iii})		1.68 (8)	2.775 (7)	161 (7)
O(W)$\cdots$O(4^{iv})		1.75 (8)	2.789 (7)	153 (6)
C(2a)$\cdots$O(5^{ii})		2.33 (7)	3.137 (8)	142 (5)

Symmetry codes: (i) x, y, z; (ii) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (iii) $1 + x, y, z$; (iv) $-\frac{1}{2} + x, \frac{3}{2} - y, -z$.

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Structure of Guanidinomethylphosphonic Acid Monohydrate, C₂H₈N₃O₃P.H₂O

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Abstract. $M_r = 171.1$, monoclinic, $C2/c$, $a = 13.222$ (4), $b = 7.502$ (3), $c = 13.936$ (5) Å, $\beta = 104.17$ (3)°, $V = 1340.3$ (9) Å³, $Z = 8$, $D_m = 1.70$ (1), $D_x = 1.70$ Mg m⁻³, $\lambda(\text{Mo }K\alpha) = 0.71069$ Å, $\mu = 0.38$ mm⁻¹, $F(000) = 720$, final $R = 0.042$ for 1581 reflexions. The guanidinomethylphosphonic acid molecule exists as a zwitterion, $(NH_2)_2^+C\text{-}NHCH_2PO_3H^-$. The C–N–C–P torsion angle is −95.9 (3)°. The molecules are held together by a network of N–H···O and O–H···O hydrogen bonds.

Introduction. Guanidinophosphonic acids (1) were recently described (Rowley, Greenleaf & Kenyon, 1971; Moreaud, Lacoste & Neuzil, 1975). They have special biological interest as the phosphonic acid analogues of arginine (2) and creatine (3).

$$
\begin{array}{c}
\underset{(1)}{
\begin{array}{c}
\text{NH} \qquad\quad \text{O} \\
\parallel \qquad\qquad \parallel \quad\diagup\text{OH} \\
\text{H}_2\text{N--C--NH--CH--P} \\
\qquad\qquad\qquad\mid \qquad\quad\diagdown\text{OH} \\
\qquad\qquad\qquad R
\end{array}}
\qquad
\underset{(2)}{
\begin{array}{c}
\text{NH} \qquad\qquad\quad \text{O} \\
\parallel \qquad\qquad\qquad \parallel \quad\diagup\text{OH} \\
\text{H}_2\text{N--C--NH--(CH}_2)_3\text{--P} \\
\qquad\qquad\qquad\qquad\qquad\diagdown\text{OH}
\end{array}}
\end{array}
$$

$$
\underset{(3)}{
\begin{array}{c}
\text{NH} \qquad\quad \text{O} \\
\parallel \qquad\qquad \parallel \quad\diagup\text{OH} \\
\text{H}_2\text{N--C--N--CH}_2\text{--P} \\
\qquad\qquad\mid \qquad\qquad\diagdown\text{OH} \\
\qquad\qquad\text{CH}_3
\end{array}}
$$

The synthesis of a series of guanidinophosphonic acids has been described both with free (Oleksyszyn, Tyka & Mastalerz, 1977) and substituted (Oleksyszyn & Tyka, 1978) guanidino groups. As a continuation of our research on the aminophosphonic acids, the X-ray structure of guanidinomethylphosphonic acid is presented in this paper.

Experimental. Clear, colourless crystals from water at room temperature, dimensions 0.2 × 0.2 × 0.3 mm; density by flotation in carbon tetrachloride/ethylene bromide; monoclinic *Cc* or *C2/c* from Weissenberg photographs, *C2/c* confirmed by refinement; Syntex *P2₁* computer-controlled four-circle diffractometer, scintillation counter, graphite monochromator; cell parameters by least squares from setting angles of 15 reflexions; 1890 independent reflexions; $2\theta_{max} = 60°$; variable θ–2θ scans, scan rate 2.0–29.3° min⁻¹, depending on intensity; two standards measured every 30 reflexions, no significant change; corrected for Lorentz and polarization, not for absorption; 1600 with $I > 1.96\sigma(I)$ used for structure determination; index range h 0 to 17, k 0 to 10, l −19 to 18; 19 reflexions showing a large $(F_o - F_c)/\sigma(F_o)$ ratio excluded in the final stages of refinement; calculations performed with Syntex (1976) *XTL* system; neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); direct methods, Syntex (1976) version of *MULTAN* (Germain, Main & Woolfson, 1971);