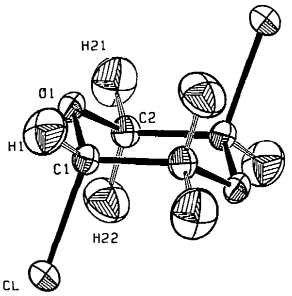

Fig. 1. *trans*-2,5-Dichloro-1,4-dioxane at 97 K. Thermal ellipsoids at 75% probability (Johnson, 1976).

It is interesting to note that the rigid-body analyses with and without the H atoms included gave very similar results with almost as good a fit. For the C—H bonds, the harmonic riding motion and anharmonic stretch corrections almost cancel at 97 K, as has been observed in other low-temperature neutron diffraction analyses (Jeffrey, 1992).

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Structure of *N*-Acetyl-L-leucyl-L-prolinamide Monohydrate

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Abstract. $C_{13}H_{23}N_3O_3.H_2O$, $M_r = 287.36$, orthorhombic, $P2_12_12_1$, $a = 6.3863$ (8), $b = 14.346$ (2), $c = 17.247$ (2) Å, $V = 1580.1$ (6) Å^3, $Z = 4$, $D_x = 1.208$ g cm^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 7.04$ cm^{-1}, $F(000) = 624$, room temperature, final $R = 0.037$ for 1693 reflections with $I \geq 2.5\sigma(I)$ and 257

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Table 1. *Positional parameters and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses for non-*H *atoms*

$$B_{eq} = (4/3)\sum_i\sum_j B_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O1	0.8456 (3)	0.2986 (1)	0.40215 (9)	4.14 (3)
O2	0.7879 (3)	0.0679 (1)	0.3964 (1)	4.78 (4)
O3	0.5309 (3)	0.4934 (2)	0.3676 (1)	4.96 (4)
N1	0.8106 (3)	0.4436 (1)	0.3006 (1)	3.20 (3)
N2	0.5543 (3)	0.2299 (1)	0.3562 (1)	3.05 (3)
N3	0.7177 (4)	0.0956 (2)	0.5222 (1)	4.75 (5)
C1	0.7166 (4)	0.3555 (2)	0.2796 (1)	2.95 (4)
C2	0.7120 (4)	0.2923 (2)	0.3512 (1)	3.00 (4)
C3	0.5192 (4)	0.1793 (2)	0.4281 (1)	3.10 (4)
C4	0.6913 (4)	0.1097 (2)	0.4466 (1)	3.34 (4)
C5	0.7172 (4)	0.5038 (2)	0.3471 (1)	3.53 (4)
C6	0.8417 (6)	0.5854 (2)	0.3734 (2)	4.91 (6)
C7	0.8360 (4)	0.3104 (2)	0.2129 (1)	3.30 (4)
C8	0.8143 (4)	0.3616 (2)	0.1357 (1)	3.74 (5)
C9	0.5903 (5)	0.3556 (3)	0.1048 (2)	5.91 (7)
C10	0.9696 (5)	0.3252 (3)	0.0762 (2)	5.98 (7)
C11	0.3052 (4)	0.1325 (2)	0.4154 (2)	4.79 (6)
C12	0.2678 (5)	0.1365 (2)	0.3321 (2)	5.98 (6)
C13	0.3837 (4)	0.2173 (2)	0.3003 (2)	4.37 (5)
O*W*	1.2223 (3)	0.4872 (2)	0.2497 (1)	8.15 (6)

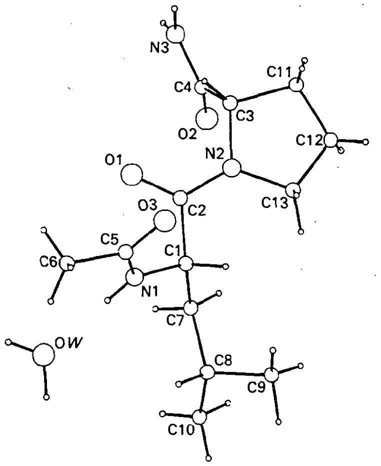

Fig. 1. Perspective view of the NALPA molecule with the atomic numbering scheme.

variables. The peptide linkage is in a *trans* conformation. The pyrrolidine ring adopts a puckered C$^\gamma$-*endo* conformation and the leucine side chain is in a twisted $[g^-(tg^-)]$ conformation. The crystal packing is stabilized by a three-dimensional network of hydrogen bonds which involve all the donor groups. The water molecule plays an important part in the crystal packing, being engaged in three hydrogen bonds with different *N*-acetylamide molecules.

Table 2. *Bond distances* (Å), *bond angles* (°) *and some torsion angles* (°) *with e.s.d.'s in parentheses*

O1—C2	1.228 (3)	C1—C7	1.523 (3)
O2—C4	1.220 (3)	C3—C4	1.518 (3)
O3—C5	1.250 (3)	C3—C11	1.539 (4)
N1—C1	1.446 (3)	C5—C6	1.485 (4)
N1—C5	1.321 (3)	C7—C8	1.527 (3)
N2—C2	1.351 (3)	C8—C9	1.529 (4)
N2—C3	1.455 (3)	C8—C10	1.520 (4)
N2—C13	1.465 (3)	C11—C12	1.458 (4)
N3—C4	1.331 (3)	C12—C13	1.480 (4)
C1—C2	1.532 (3)		
C1—N1—C5	122.5 (2)	O2—C4—N3	123.8 (2)
C2—N2—C3	120.0 (2)	O2—C4—C3	122.7 (2)
C2—N2—C13	126.5 (2)	N3—C4—C3	113.4 (2)
C3—N2—C13	112.6 (2)	O3—C5—N1	121.6 (2)
N1—C1—C2	108.8 (2)	O3—C5—C6	121.1 (2)
N1—C1—C7	110.6 (2)	N1—C5—C6	117.3 (2)
C2—C1—C7	111.5 (2)	C1—C7—C8	114.1 (2)
O1—C2—N2	121.4 (2)	C7—C8—C9	111.2 (2)
O1—C2—C1	121.4 (2)	C7—C8—C10	111.4 (2)
N2—C2—C1	117.2 (2)	C9—C8—C10	110.8 (2)
N2—C3—C4	113.3 (2)	C3—C11—C12	105.6 (2)
N2—C3—C11	103.5 (2)	C11—C12—C13	108.3 (2)
C4—C3—C11	112.7 (2)	N2—C13—C12	103.0 (2)
C5—N1—C1—C2	−69.1 (3)	N1—C1—C2—N2	149.6 (2)
C5—N1—C1—C7	168.0 (2)	C7—C1—C2—N2	−88.1 (2)
C1—N1—C5—C6	171.4 (2)	N1—C1—C7—C8	−68.9 (2)
C3—N2—C2—O1	10.3 (3)	N2—C3—C4—N3	150.7 (2)
C3—N2—C2—C1	−169.4 (2)	N2—C3—C11—C12	16.5 (3)
C2—N2—C3—C4	−68.8 (3)	C1—C7—C8—C9	−67.2 (3)
C13—N2—C3—C11	−0.9 (3)	C1—C7—C8—C10	168.6 (2)
C3—N2—C13—C12	−14.7 (3)	C3—C11—C12—C13	−26.6 (3)
N1—C1—C2—O1	−30.0 (3)	C11—C12—C13—N2	25.4 (3)

Introduction. This work is part of studies on the solid-state properties and thermodynamic behaviour of uncharged amino-acid and peptide derivatives (*N*-acetylamides). Knowledge of these crystal structures is helpful in the rationalization of entropies and enthalpies of melting, sublimation and solid–solid phase transitions (Puliti, Mattia, Barone & Giancola, 1989, 1991; Puliti, Mattia, Barone, Della Gatta & Ferro, 1990). Structural studies on oligopeptides bearing the prolyl residue are of considerable interest since the pyrrolidine ring imposes restrictions on the conformations of the adjacent residues and also influences the secondary structure of proteins.

Experimental. Single crystals of *N*-acetyl-L-leucyl-L-prolinamide (NALPA) (Milburn, 1984; Lilley, 1988) monohydrate were grown as colourless prisms by slow evaporation from ethyl ether solution. A sample of size 0.75 × 0.16 × 0.12 mm was used; Enraf–Nonius CAD-4F diffractometer, graphite-monochromated Cu $K\alpha$ radiation, room temperature. Cell parameters from 25 reflections with $20 < \theta < 23°$, ω–2θ scan as suggested by peak-shape analysis. Four standard reflections monitored every 4 h (4% variation), no significant decay; 1828 reflections with $\theta \le 73°$ were measured, $0 \le h \le 7$, $0 \le k \le 17$, $0 \le l \le 21$, 1693 with $I \ge 2.5\sigma(I)$; Lp correction, absorption ignored. Structure solved by *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Anisotropic full-matrix refinement (on F), H-atom positions refined, with B equal to that of the parent atom, final $R = 0.037$, $wR = 0.042$. Function minimized $\sum w(\Delta F)^2$, $w^{-1} = [\sigma^2(F_o) + (0.02F_o)^2 + 2]$ (Killean & Lawrence, 1969) and σ from counting statistics. A correction for secondary extinction (Stout & Jensen, 1968) was refined [g coefficient = $3.9(2) \times 10^{-6}$], $S = 0.74$; final $(\Delta/\sigma)_{\max} = 0.03$; $-0.17 \le \Delta\rho \le 0.23$ e Å^{-3}. Scattering factors from

International Tables for X-ray Crystallography (1974, Vol. IV), Enraf–Nonius *SDP* software (B. A. Frenz & Associates, Inc., 1985), MicroVAX 3100 computer. Final atomic parameters for the non-H atoms are listed in Table 1,* the atomic numbering scheme is given in Fig. 1.

Discussion. Fig. 1 shows a view of the molecule approximately perpendicular to the peptide plane. Geometrical parameters are given in Table 2. On average, bond lengths and bond angles agree with the generally accepted values for this kind of compound (Puliti, Mattia, Barone & Giancola, 1991, and references therein). The long N2—C2 distance [1.351 (3) Å], compared with N1—C5 [1.321 (3) Å], is consistent with the value accepted for the N—C bond in the presence, or absence, of Pro residues (Momany, McGuire, Burgess & Scheraga, 1975).

The peptide linkage between Leu and Pro residues is in a distorted *trans* conformation [C1—C2—N2—C3 = − 169.4 (2)°]. The geometry of the peptide group preceding the *trans*-proline agrees with mean values found in similar derivatives (Benedetti, 1982). Owing to the steric hindrance of the pyrrolidine ring, the bond angle C2—N2—C13 is significantly larger than C2—N2—C3 [126.5 (2) against 120.0 (2)°].

Both torsion-angle pairs, φ_1, ψ_1 and φ_2, ψ_2, fall in the *F* region of the Zimmerman map (Zimmerman, Pottle, Némethy & Scheraga, 1977) and indicate that the molecular backbone is in a collagen-like helix conformation. The NALPA conformation closely resembles that of L-leucyl-L-prolylglycine (Marsh, 1980). The rather flexible pyrrolidine ring (Madison, 1977), whose conformation is often governed by packing interactions, adopts in this structure a C^{γ}-*endo* puckered conformation (Trikha, Patel & Singh, 1990, and references therein). C^{γ} puckering has been described (Venkatachalam, Price & Krimm, 1974) as the most favoured conformation, whenever the θ torsion angle is near 0° [C13—N2—C3—C11 = −0.9 (3)°]. There is no indication of the conformational disorder observed in several proline rings of peptides (Panneerselvam, Chacko & Veena, 1990).

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···A	D···A	H···A	D—H···A
N1—H1···OW^{i}	2.842 (3)	2.00 (3)	177 (2)
N3—H2···$O1^{ii}$	3.107 (3)	2.27 (3)	151 (3)
N3—H3···$O3^{iii}$	3.040 (3)	2.32 (3)	139 (3)
OW—H′···$O2^{iv}$	2.774 (3)	1.83 (4)	167 (4)
OW—H″···$O3^{v}$	2.833 (3)	2.02 (4)	163 (4)

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

The Leu side chain is in the $[g^{-}(tg^{-})]$ conformation, as for *N*-acetyl-L-leucinamide (Puliti, Mattia, Barone & Giancola, 1989). This twisted conformation is energetically favoured, together with the extended conformation $[t(g^{+}t)]$, and they are the only conformations observed in crystals of small peptides (Benedetti, Morelli, Némethy & Scheraga, 1983). Both peptide groups are approximately planar.

Crystal packing is stabilized by a network of intermolecular hydrogen bonds involving all donor groups (see Fig. 2 and Table 3). Water H atoms are engaged with the amidic O2 and the acetyl O3 atoms of two different molecules, while O*W* accepts a third hydrogen bond from the N1—H group of Leu. Moreover the molecules, related by a screw axis parallel to the *a* axis, are linked together by two weaker hydrogen bonds, between the terminal amide group (NH_2) and the carbonyl O1 and O3 atoms. The short intermolecular contact C3···O1 = 3.146 (3) Å [C3—H5···O1 = 128 (2)° and H5···O1 = 2.39 (3) Å] could reveal a C—H···O hydrogen bond (Taylor & Kennard, 1982).

Fig. 2 shows the molecular packing projected along the *a* axis. Most polar groups (except O1) lie approximately in a plane normal to the *b* axis, while the two apolar side chains and the methyl of the acetyl residue settle in a region around a screw axis along *a* ($y = 0.75$, $z = 0.5$ in Fig. 2) with weak van der Waals interactions [≥ 3.603 (3) Å]. The packing is characterized by alternation of polar and apolar regions, which is a common feature of this type of compound.

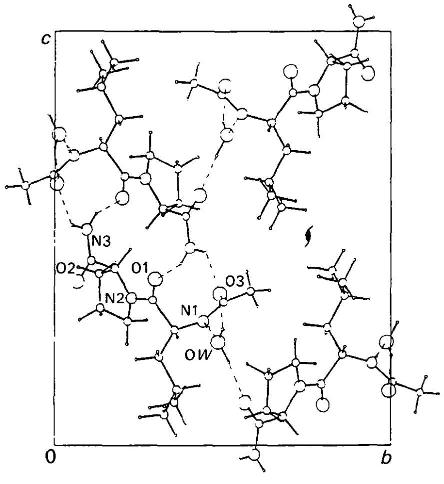

Fig. 2. Crystal packing projected along the *a* axis. Only atoms involved in hydrogen bonds are numbered. Dashed lines indicate hydrogen bonds.

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* List of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54671 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0277]

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Structure of 4-Bromochalcone

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Abstract. 3-(4-Bromophenyl)-1-phenyl-2-propen-1-one, $C_{15}H_{11}BrO$, $M_r = 287.16$, monoclinic, Cc, $a = 29.027\ (7)$, $b = 7.26\ (2)$, $c = 5.917\ (3)$ Å, $\beta = 101.38\ (3)°$, $V = 1222\ (3)$ Å^3, $Z = 4$, $D_x = 1.56\ \text{g cm}^{-3}$, $\lambda(\text{Mo}\ K\alpha) = 0.71073$ Å, $\mu = 33.07\ \text{cm}^{-1}$, $F(000) = 576$, $T = 296$ K, final $R = 0.058$ for 618 observed reflections with $I > 3\sigma(I)$. The structure of the title compound is non-centrosymmetric. The torsion angle O—C(3)—C(2)—C(1) of the central C_2H_2CO group is −16°. The dihedral angle between the two phenyl rings is 48.4°. The conjugated system of the molecule is disturbed.

Introduction. The title compound is a newly developed organic crystal with non-linear optical properties. The second harmonic generation (SHG) intensity of the compound, measured on a powder sample, is seven times larger than that of the urea standard (Goto, 1989). In order to explore the relationship between its structure and non-linear optical properties, we synthesized the title compound and determined its structure.

Experimental. The title compound was prepared by acyloin condensation of 4-bromobenzaldehyde with acetophenone at room temperature (Migrdichian, 1957). The crystals were obtained from ethanol solution. A colorless transparent needle crystal with approximate dimensions 2.0 × 0.1 × 0.1 mm was mounted on a glass fiber in a random orientation. Preliminary examination and intensity data collection were performed on an AFC-5 diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Cell constants from 20 reflections, $18 < 2\theta < 22°$. Space group determined to be Cc from systematic absences and from the absence of a center of symmetry (as required by the non-linear optical properties of the crystal). A total of 1341 reflections were collected, of which 1314 were unique. Data were collected in the range $1 < \theta < 26°$ ($0 < h < 36$, $0 < k < 9$, $-7 < l < 7$) by ω–2θ scan technique, ω-scan width $(1.5 + 0.3\tan\theta)°$, scan speed 16° min^{-1}. 631 observed reflections with $I > 3\sigma(I)$ were used for structure determination. Three standard reflections ($3\bar{3}\bar{1}$, $\overline{12},\bar{2},0$, $\bar{7}\bar{3}0$) were measured every 150 measurements and showed no significant intensity fluctuation. Lorentz and polarization corrections were applied. The linear absorption coefficient is 33.07 cm^{-1} for Mo $K\alpha$ radiation. *DIFABS* (Walker & Stuart, 1983) empirical absorption corrections were applied, yielding relative transmission coefficients ranging from 0.6394 to 1.3808.

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