Bond lengths and valence angles of the title compound are listed in Table 2; they have not been corrected for effects of thermal motion. The average free molecule in the conformation stated above would have C_2 symmetry with the twofold axis going through the centre of C(1)—C(7) and bisecting the phenyl interplanar angle. This symmetry is roughly displayed in the bond lengths and valence angles found in the crystal. If one, however, looks at the distances of the various atoms from the ring planes, significant deviations from twofold symmetry occur, for instance C(1) and C(7) 0·072 and 0·141 Å and Cl(2) and Cl(5) 0·061 and 0·009 Å (see Table 1). Further inspection of Table 2 shows the *ortho* and *meta* C—Cl bonds to be shorter than the *para* C—Cl bonds, and reveals the inequivalence of various distances and angles within one phenyl ring. The *para* C—Cl bonds (mean 1·737 Å) are close to the standard C—Cl length [1·740 (1) Å] (Domenicano, Vaciago & Coulson, 1975). Deviations from D_{6h} symmetry in the phenyl rings are significant but complex. A detailed analysis of the endocyclic valence angles according to Domenicano & Murray-Rust (1979) cannot be made due to lack of knowledge of the parameters pertaining to a trichlorophenyl substituent, which is not coplanar with the phenyl group and hence weakly conjugated.

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Structure of (*Z*)-*N*-Benzoyl-α,β-dehydroleucine

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Abstract. $C_{13}H_{15}NO_3$, $M_r = 233{\cdot}27$, triclinic, $P\bar{1}$, $a = 22{\cdot}914\ (4)$, $b = 11{\cdot}282\ (3)$, $c = 5{\cdot}056\ (2)$ Å, $\alpha = 95{\cdot}30\ (5)$, $\beta = 93{\cdot}04\ (5)$, $\gamma = 95{\cdot}13\ (5)°$, $V = 1293{\cdot}8\ (7)$ Å^3, $Z = 4$, $D_x = 1{\cdot}198$, $D_m = 1{\cdot}170$ g cm^{-3} (by flotation in aqueous KBr solution), Mo $K\alpha$ radiation (monochromatized by a graphite plate), $\lambda = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 0{\cdot}797$ cm^{-1}, $F(000) = 496$, $T = 298$ K, $R = 5{\cdot}54\%$ for 3106 reflections with $I > 3\sigma(I)$. There are two independent molecules in the asymmetric unit. They are approximate enantiomers $\{\varphi[\text{C(O}_2\text{)—C—N—C}] = -51{\cdot}7$, $\psi[\text{N—C—C—O(H)}] = -29{\cdot}6°$ for molecule A; $\varphi = 55{\cdot}9$, $\psi = 25{\cdot}8°$ for molecule $B\}$ linked in pairs by hydrogen bonds through the carboxylic groups.

Introduction. α,β-Unsaturated amino-acid derivatives are present in many natural peptides, several of which exhibit biological activities (Ajò, Granozzi, Tondello & Del Pra, 1980, and references therein). The α,β-double bond in dehydro-amino-acid derivatives represents, in addition to the amino and carboxy groups, the introduction of a third reactive function into the molecule, which makes this class of compounds particularly interesting because of their unusual conformational and electronic features (Ajò, Casarin, Bertoncello, Busetti, Ottenheijm & Plate, 1985, and references therein).

Conformational studies of α,β-unsaturated amino-acid derivatives are of interest not only from a biological point of view, but also in order to investigate the mechanism of their asymmetric hydrogenation

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(Ajò, Busetti, Ottenheijm & Plate, 1984, and references therein).

In previous papers we reported upon the crystal and molecular structure of *N*-acetyldehydroalanine (Ajò, Granozzi, Tondello, Del Pra & Zanotti, 1979), *N*-acetyldehydrophenylalanine (Ajò, Casarin, Granozzi & Busetti, 1981) and its ethyl ester (Ajò, Busetti, Ottenheijm & Plate, 1984), *N*-acetyldehydroproline (Ajò, Busetti, Granozzi & Liakopoulou-Kyriakides, 1984), and several cyclic (Ajò, Casarin, Bertoncello, Busetti, Ottenheijm & Plate, 1985) and acyclic (Ajò, Busetti & Granozzi, 1982; Busetti, Ajò & Casarin, 1984) α,β-unsaturated dipeptides. In particular, these theoretical and experimental studies of *N*-acyldehydroamino acids and esters stressed their high conformational flexibility.

As a further contribution to the knowledge of the conformational effects of different side chains we present here a study of the molecular and crystal structure of (*Z*)-*N*-benzoyl-α,β-dehydroleucine.*

Experimental. Philips PW 1100 four-circle diffractometer (graphite-monochromatized Mo $K\alpha$ radiation). For data collection a needle-shaped crystal $0{\cdot}05 \times 0{\cdot}05 \times 0{\cdot}20$ mm was used, θ–2θ scan mode, scan width 1·4°, scan speed $0{\cdot}035°\ \mathrm{s}^{-1}$, background measured for 10 s at each extremity, $2° < \theta < 28°$, three standard intensity reflections ($\bar{7}01$, 440 and 531), measured at 3 h intervals, no significant variation. Unit cell: least-squares refinement of 20 high-angle θ values. Lorentz–polarization correction, no absorption correction. Of 6246 independent collected reflections, 3106 had $I > 3\sigma(I)$. $R_{\text{int}} = 2{\cdot}81\%$. Structure solved by direct methods, E map revealed all non-hydrogen atoms. Full-matrix least-squares refinement (on F), unit weights. Methyl H atoms in staggered calculated positions; carboxylic H atoms not determined; all other H atoms localized on a difference map and refined in the last cycle of least squares. Residual peaks in final difference map from 0·19 to $-0{\cdot}16\ \mathrm{e\ Å^{-3}}$. No correction for secondary extinction. The refinement converged to $R = 5{\cdot}54\%$, $wR = 5{\cdot}54\%$, $S = 0{\cdot}73$, mean $\Delta/\sigma = 0{\cdot}03$, max. $\Delta/\sigma = 0{\cdot}07$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs: *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), *SHELX*76 (Sheldrick, 1976) and *ORTEP*II (Johnson, 1976).

Table 1. *Fractional positional parameters* ($\times 10^4$) *and equivalent isotropic thermal parameters* (*e.s.d.'s in parentheses*)

$$B_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Molecule *A*				
O(1)	1903 (1)	7371 (2)	7174 (5)	4·83 (8)
O(2)	2473 (1)	8993 (2)	6387 (5)	4·55 (8)
O(3)	1514 (1)	10303 (2)	8539 (4)	4·70 (8)
N(1)	1508 (1)	9917 (2)	4094 (5)	3·30 (7)
C(1)	1985 (2)	8306 (3)	6097 (7)	3·64 (10)
C(2)	1512 (2)	8676 (3)	4284 (6)	3·31 (9)
C(3)	1144 (2)	7849 (3)	2906 (7)	3·88 (10)
C(4)	641 (2)	8033 (4)	998 (8)	4·85 (12)
C(5)	161 (3)	8575 (6)	2412 (12)	9·50 (25)
C(6)	429 (2)	6892 (5)	−647 (11)	7·88 (21)
C(7)	1519 (2)	10684 (3)	6336 (6)	3·39 (9)
C(8)	1531 (2)	11976 (3)	6015 (7)	3·53 (9)
C(9)	1227 (2)	12409 (3)	3920 (8)	4·56 (12)
C(10)	1242 (2)	13631 (4)	3783 (10)	6·32 (16)
C(11)	1568 (3)	14412 (4)	5660 (11)	6·77 (17)
C(12)	1880 (3)	13985 (4)	7715 (10)	6·52 (16)
C(13)	1855 (2)	12770 (4)	7927 (8)	4·94 (12)
Molecule *B*				
O(1)	3218 (1)	8248 (2)	9918 (5)	4·48 (7)
O(2)	2626 (1)	6647 (2)	10682 (5)	4·90 (7)
O(3)	3603 (1)	5221 (2)	8817 (4)	4·86 (8)
N(1)	3530 (1)	5687 (2)	13185 (5)	3·52 (7)
C(1)	3122 (2)	7319 (3)	11005 (7)	3·65 (10)
C(2)	3575 (2)	6923 (3)	12878 (6)	3·33 (9)
C(3)	3968 (2)	7720 (3)	14190 (7)	3·95 (10)
C(4)	4462 (2)	7487 (4)	16101 (8)	4·89 (12)
C(5)	4940 (3)	6938 (6)	14635 (12)	9·48 (25)
C(6)	4694 (2)	8617 (5)	17806 (10)	6·71 (17)
C(7)	3530 (2)	4881 (3)	11031 (6)	3·47 (10)
C(8)	3440 (2)	3589 (3)	11433 (7)	3·51 (9)
C(9)	3690 (2)	2781 (4)	9724 (8)	5·15 (13)
C(10)	3606 (3)	1566 (4)	9992 (11)	6·79 (18)
C(11)	3261 (3)	1161 (4)	11943 (11)	6·65 (18)
C(12)	3012 (2)	1953 (4)	13612 (9)	5·60 (15)
C(13)	3101 (2)	3173 (3)	13402 (8)	4·39 (12)

Discussion. Final positional parameters are reported in Table 1.† Bond distances and angles are shown in Table 2 and the numbering scheme of the atoms is reported in the *ORTEP*II projection (Fig. 1). Four molecules are to be arranged in the unit cell, so the asymmetric unit consists of two independent molecules (*A* and *B*). Bond distances are within the usual range for dehydroamino-acid derivatives: in particular, the N—C$_\alpha$ bond length is 1·413 (4) Å (for molecule *A*) and 1·412 (4) Å (for molecule *B*), to be compared with those reported for dehydro-Ala-OH [1·409 (5) Å] (Ajò, Granozzi, Tondello, Del Pra & Zanotti, 1979) and dehydro-Phe-OH [1·438 (6) Å] (Ajò, Casarin, Granozzi & Busetti, 1981).

The conformation of both independent molecules $\{\varphi[\mathrm{C(1)–C(2)–N(1)–C(7)}] = -51{\cdot}7\ (5)$, $\psi[\mathrm{N(1)–C(2)–C(1)–O(2)}] = -29{\cdot}6\ (6)$, $\omega[\mathrm{C(2)–N(1)–C(7)–C(8)}] = 178{\cdot}3\ (4)°$ for molecule *A*, $\varphi = 55{\cdot}9\ (5)$, $\psi = 25{\cdot}8\ (6)$, $\omega = -175{\cdot}8\ (4)°$ for molecule $B\}$ corresponds to a minimum-energy region in the conformational maps (ω = *trans*) of β-substituted α,β-unsaturated amino-acid derivatives (Ajò, Casarin, Granozzi & Busetti, 1981; Ajò, Casarin & Granozzi, 1982) and it is similar to that previously reported for (*Z*)-*N*-acetyldehydrophenylalanine (Ajò, Casarin, Granozzi & Busetti, 1981). It is noteworthy that in *N*-*tert*-butoxycarbonyldehydroleucine (Chauhan, Stammer, Norskov-

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* 2-Benzoylamino-4-methyl-2-pentenoic acid.

† Lists of structure factors, anisotropic thermal parameters and coordinates of hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42889 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Lauritzen & Gary Newton, 1979) the value of ψ indicates a *transoid* conformation [a similar behaviour has been found in the case of *N*-acetyldehydrophenylalanine and its ethyl ester (Ajò, Busetti, Ottenheijm & Plate, 1984)] and the value of ω indicates a *cisoid* one; moreover, the crystal structure of the title compound contains two independent molecules which assume different conformations [this is a usual feature of this class of compounds (Chauhan, Stammer, Norskov-Lauritzen & Gary Newton, 1979; Ajò, Busetti, Ottenheijm & Plate, 1984; Ajò, Casarin, Bertoncello, Busetti, Ottenheijm & Plate, 1985)]; these are further evidence of the significant conformational flexibility of α,β-unsaturated amino-acid derivatives.

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

	Molecule *A*	Molecule *B*
O(1)–C(1)	1·235 (4)	1·236 (5)
O(2)–C(1)	1·296 (5)	1·303 (5)
O(3)–C(7)	1·231 (4)	1·231 (4)
N(1)–C(2)	1·413 (4)	1·412 (4)
N(1)–C(7)	1·359 (4)	1·353 (4)
C(1)–C(2)	1·495 (6)	1·494 (6)
C(2)–C(3)	1·321 (5)	1·320 (5)
C(3)–C(4)	1·505 (6)	1·506 (6)
C(4)–C(5)	1·489 (8)	1·502 (8)
C(4)–C(6)	1·494 (7)	1·509 (6)
C(7)–C(8)	1·479 (5)	1·488 (5)
C(9)–C(10)	1·384 (6)	1·387 (6)
C(9)–C(8)	1·387 (6)	1·381 (6)
C(10)–C(11)	1·374 (7)	1·381 (9)
C(11)–C(12)	1·378 (8)	1·356 (7)
C(12)–C(13)	1·381 (6)	1·388 (6)
C(13)–C(8)	1·390 (5)	1·385 (6)
C(2)–N(1)–C(7)	120·1 (3)	120·0 (3)
O(1)–C(1)–O(2)	123·6 (4)	123·5 (4)
O(2)–C(1)–C(2)	116·6 (3)	115·8 (3)
O(1)–C(1)–C(2)	119·8 (4)	120·8 (4)
N(1)–C(2)–C(1)	116·3 (3)	115·7 (3)
C(1)–C(2)–C(3)	119·5 (4)	119·8 (3)
N(1)–C(2)–C(3)	124·2 (4)	124·5 (4)
C(2)–C(3)–C(4)	127·7 (4)	127·3 (4)
C(3)–C(4)–C(6)	110·8 (4)	110·9 (4)
C(3)–C(4)–C(5)	111·4 (4)	110·7 (5)
C(5)–C(4)–C(6)	112·3 (5)	111·6 (5)
O(3)–C(7)–N(1)	120·4 (3)	120·2 (3)
N(1)–C(7)–C(8)	117·6 (3)	118·0 (3)
O(3)–C(7)–C(8)	121·9 (3)	121·8 (3)
C(10)–C(9)–C(8)	119·5 (4)	120·3 (5)
C(9)–C(10)–C(11)	120·5 (5)	119·9 (5)
C(10)–C(11)–C(12)	120·2 (5)	119·9 (5)
C(11)–C(12)–C(13)	120·0 (5)	120·9 (5)
C(12)–C(13)–C(8)	120·0 (4)	119·7 (4)
C(9)–C(8)–C(13)	119·8 (4)	119·3 (4)
C(7)–C(8)–C(13)	117·8 (4)	122·2 (4)
C(7)–C(8)–C(9)	122·4 (4)	118·4 (4)

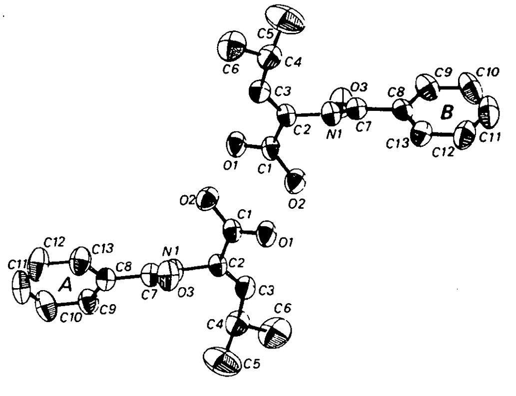

Fig. 1. *ORTEP*II projection of the title compound with atom-numbering scheme.

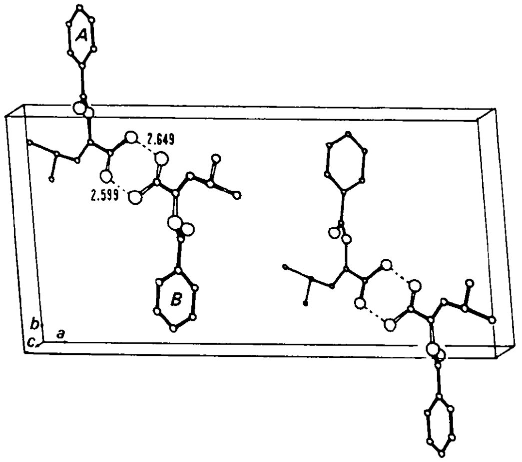

Fig. 2. The crystal packing of the title compound.

Crystal packing is given in Fig. 2. Molecules *A* and *B* are linked in pairs (through a pseudo-inversion centre at 0·25, 0·78, 0·86) by hydrogen bonds connecting the carboxylic groups: O(1)–O′(2) = 2·599 (4), O′(1)–O(2) = 2·649 (4) Å; the single prime refers to molecule *B*. These values are to be compared to those of *N*-*tert*-butoxycarbonyldehydroleucine, O(1)–O(2) = 2·64 Å (average values for the two units) (Chauhan, Stammer, Norskov-Lauritzen & Gary Newton, 1979). The six-membered ring closed by hydrogen bonds is planar: C(1) is −0·057 (4) and C′(1) is +0·057 (4) Å out of the plane through the four oxygen atoms, whose deviations are ±0·007 (3) Å. Moreover, molecules are linked along the *c* axis by two series of hydrogen bonds:

	r(N···O)	∠N–H···O	
N(1)–H···O(3)	2·882 (3) Å	155 (3) °	($x, y, z-1$)
N′(1)–H′···O′(3)	2·942 (4)	165 (3)	($x, y, z+1$).

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Structural Studies of Radical Reaction Products. II.* 2,4-Bis(4-chlorophenyl)-5,5-dimethyl-3-pyrazolidinone

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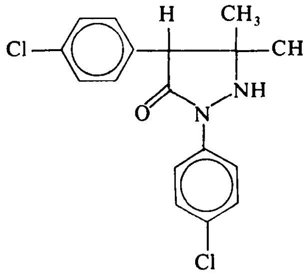
Abstract. $C_{17}H_{16}Cl_2N_2O$, $M_r = 335{\cdot}23$, triclinic, $P\bar{1}$, $a = 12{\cdot}280\,(3)$, $b = 10{\cdot}191\,(3)$, $c = 6{\cdot}633\,(2)$ Å, $\alpha = 83{\cdot}93\,(7)$, $\beta = 100{\cdot}05\,(8)$, $\gamma = 87{\cdot}70\,(8)°$, $U = 811{\cdot}3\,(5)$ Å^3, $Z = 2$, $D_x = 1{\cdot}37$ Mg m^{-3}, $\lambda(\text{Mo}\,K\bar{\alpha}) = 0{\cdot}71069$ Å, $\mu(\text{Mo}\,K\bar{\alpha}) = 0{\cdot}402$ mm^{-1}, $F(000) = 348$, room temperature, $R = 0{\cdot}056$ for 2285 observed reflections, $S = 0{\cdot}85$. The title compound, which shows pharmacological activity *in vitro*, presents a puckered pyrazolidinone ring [puckering angle 36·0 (2)°] with an N—N bond [1·445 (4) Å] longer than those usually found in hydrazidic moieties. Geometric and electronic features of this part of the molecule have a close similarity with those of antipyrine, a 3*H*-pyrazol-3-one derivative used as an antiinflammatory drug.

Introduction. During our systematic studies of homolytic reactions of arenediazonium salts we have obtained new compounds resulting from the addition of carbon free radicals to the terminal N atom of the diazonium cation (Citterio, Minisci & Vismara, 1982; Albinati, Ganazzoli & Citterio, 1983; Citterio, Ramperti & Vismara, 1981). An X-ray structural determination of the title compound confirmed the structure of the product (1) obtained from decomposition of 4-chlorobenzenediazonium chloride by Ti^{III} ions in the presence of 3-methyl-2-butenoic acid. Compounds belonging to this class of 2,4-diaryl-3-pyrazolidinones have shown antiinflammatory activity *in vitro*.



(1)

Experimental. Prismatic colourless crystals obtained from ethyl acetate solution. Single crystal of approximate dimensions 0·35 × 0·25 × 0·20 mm. Philips PW 1100 diffractometer, graphite-monochromated radiation. Cell constants determined from least-squares fit of 20 high-order reflections ($22 \leq 2\theta \leq 43°$). $\omega/2\theta$ scan technique, scan speed 0·08° s^{-1}, scan width 1·20°, background measured for 6 s on each side of the peaks, $2\theta_{\max} = 50°$ ($h \pm 14$, $k \pm 12$, l 0–7), two standard reflections (111 and $\bar{1}\bar{1}\bar{1}$) every 120 min, no significant

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* Part I: Albinati, Ganazzoli & Citterio (1983).

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