Table 2. *Bond lengths* (Å) *and angles* (°) ($\sigma = 0.01$ Å *for* C–I *and* ~0·02 Å *for other bonds*)

I–C(1)	2·10	C(2)–C(9)	1·53
C(1)–C(2)	1·38	C(9)–C(10)	1·56
C(2)–C(3)	1·41	C(10)–C(10′)	1·53
C(3)–C(4)	1·37	C(10)–C(11)	1·53
C(4)–C(5)	1·43	C(7)–O(1)	1·46
C(5)–C(6)	1·40	C(8)–O(2)	1·43
C(6)–C(1)	1·38	C(11)–O(3)	1·40
C(4)–O(1)	1·37	C(12)–O(3)	1·41
C(5)–O(2)	1·34		
C(1)–C(2)–C(3)	117	C(2)–C(1)–I	122
C(2)–C(3)–C(4)	123	C(6)–C(1)–I	116
C(3)–C(4)–C(5)	120	C(1)–C(2)–C(9)	124
C(4)–C(5)–C(6)	117	C(3)–C(2)–C(9)	119
C(5)–C(6)–C(1)	122	C(3)–C(4)–O(1)	128
C(6)–C(1)–C(2)	122	C(5)–C(4)–O(1)	113
C(2)–C(9)–C(10)	115	C(4)–C(5)–O(2)	117
C(9)–C(10)–C(11)	110	C(6)–C(5)–O(2)	127
C(9)–C(10)–C(10′)	113	C(4)–O(1)–C(7)	116
C(10′)–C(10)–C(11)	113	C(5)–O(2)–C(8)	116
C(10)–C(11)–O(3)	110	C(11)–O(3)–C(12)	113

dihedral angles C(9)–C(10)–C(10′)–C(9′) and C(11)–C(10)–C(10′)–C(11′) of −156 and −46° respectively (−180 and −60° for ideal staggered, and −120 and 0° for ideal eclipsed conformations).

Bond lengths (Table 2) are close to normal values; mean lengths are C–I 2·10, C(sp^2)–C(sp^2) 1·39, C(sp^2)–C(sp^3) 1·53, C(sp^3)–C(sp^3) 1·54, C(sp^2)–O 1·35, C(sp^3)–O 1·43 Å. The angles (Table 2) show some deviations from normal values, particularly those involving the substituents of the aromatic rings. C(2)–C(1)–I, 122, and C(1)–C(2)–C(9), 124°, suggest repulsion between the I and C(9) substituents (in accord with the displacements from the aromatic plane), but C(5)–C(4)–O(1), 113, and C(4)–C(5)–O(2), 117°, deviate from 120° in the opposite sense.

Intermolecular distances correspond to normal van der Waals interactions; the shortest of each type are: I···I 3·84, I···O 3·89, C···C 3·62, C···O 3·43 Å, and between other atom types, >3·9 Å.

We thank the National Research Council of Canada for financial support, the Royal Society for a grant to KVKR, and the University of British Columbia Computing Centre for assistance.

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Acta Cryst. (1977). B**33**, 1280–1283

DL-Leucylglycylglycine (Lgg)

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(*Received* 3 *November* 1976; *accepted* 17 *December* 1976)

Abstract. $C_{10}N_3O_4H_{19}$, monoclinic, $P2_1/c$, a = 11·52 (2), b = 12·44 (2), c = 9·70 (1) Å, β = 102·6 (2)°, $Z = 4$, $D_c = 1.26$, $D_m = 1.28$ g cm^{-3}, [λ(Cu $K\alpha$) = 1·5418 Å]. The molecules are packed head-to-tail in rows parallel to **b**. The peptide is in a *trans* configuration and an extended conformation with the terminal carboxyl group nearly parallel to the peptide plane. The side chain of the leucyl residue is in a different conformation from that normally found.

Introduction. Single crystals were obtained by slow evaporation from an ethanol–dioxane mixture. Crystals were frequently twinned; only one was untwinned and large enough for structure analysis. Cell dimensions were determined from rotation and Weissenberg photographs and the intensities collected by the equi-inclination Weissenberg technique for hkl, l = 0–4, with the multiple-film method. The intensities were estimated visually and corrected for Lorentz, polarization and absorption factors. 750 reflexions were possible of which only 570 had observable intensities. Photographs about **b** or **a** could not be taken

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Table 1. *Fractional coordinates* ($\times 10^4$) *with standard deviations in parentheses*

	x	*y*	*z*
N(1)	3769 (12)	621 (9)	2831 (17)
C(1)	2880 (16)	1382 (11)	3059 (14)
C(2)	2962 (17)	2487 (19)	2210 (18)
O(1)	3151 (18)	2497 (13)	1075 (13)
N(2)	2971 (12)	3355 (9)	3072 (16)
C(3)	3273 (18)	4458 (12)	2537 (22)
C(4)	3520 (14)	5197 (12)	3839 (19)
O(2)	3561 (13)	4841 (10)	5025 (8)
N(3)	3668 (12)	6255 (9)	3552 (12)
C(5)	3951 (18)	6981 (11)	4851 (21)
C(6)	3755 (14)	8198 (11)	4420 (20)
O(3)	3400 (13)	8461 (7)	3152 (12)
O(4)	4026 (9)	8838 (7)	5451 (14)
C(7)	1584 (18)	893 (14)	2096 (16)
C(8)	439 (27)	1528 (20)	2436 (38)
C(9)	9374 (22)	1102 (10)	1244 (10)
C(10)	326 (12)	1527 (19)	3885 (18)

since the crystal was needle-shaped and could not be cut. The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). 150 reflexions with $E \geq 1{\cdot}5$ were used for sign determination. One of the *E* maps gave the positions of 13 non-hydrogen atoms and the remaining atoms were located from difference maps. The structure was refined by full-matrix least-squares with *ORFLS* (Busing, Martin & Levy, 1962) which minimizes $\Sigma\omega(|F_o| - k|F_c|)^2$. No attempts were made to locate H atoms. At later stages of refinement weights $\omega = 1/(0{\cdot}8 + 0{\cdot}06\,F_o)$, an extinction correction and individual anisotropic temperature factors were used. The refinement was stopped when *R* was 0·092 for the 570 reflexions.

Discussion. The atomic coordinates are listed in Table 1.* The standard deviations of some of the distances are quite large, as is to be expected from the large thermal vibrations. Such unusually large thermal vibrations in peptides with leucine have been reported in D-leucylglycine hydrobromide (Rao, 1969), L-leucine hydrobromide (Subramanian, 1967), glycyl-L-leucyl-L-tyrosine (Franks & van der Helm, 1971), *S*-benzyl-L-cysteinyl-L-prolyl-L-leucylglycinamide (Rudko & Low, 1975) and DL-leucylglycine ethyl ester (Timmins, 1975).

The structure projected down **c** is shown in Fig. 1. The molecules are packed in rows, approximately parallel to **b** in a head-to-tail fashion. There are five protons which can take part in hydrogen-bonding and all are involved in intermolecular bonds. The possible hydrogen bonds are indicated in Fig. 1 and the distances and angles involved are summarized in Table 2. The terminal NH_3^+ group forms three hydrogen bonds with the O atoms of the carboxyl and leucylglycyl peptide groups. The H atoms attached to the peptide N(3) form hydrogen bonds with O(1) and O(4) of the neighbouring molecules. The peptide N atoms are nearly plane trigonal. Marsh & Donohue (1967) have observed that hydrogen bonds involving the amide N atoms as donors are significantly longer than those involving the terminal NH_3^+ group. Lgg shows the same behaviour.

The bond angles and distances in the backbone of the peptide and the side group are listed in Table 3. In

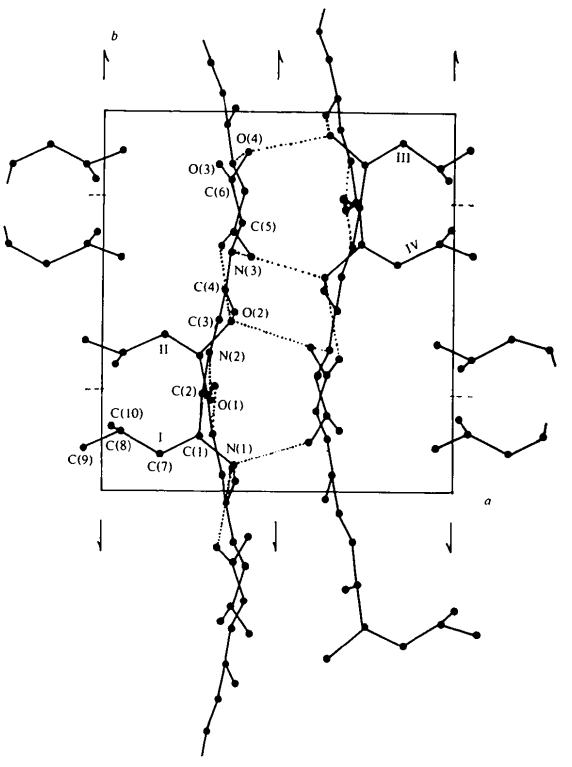

Fig. 1. The crystal structure viewed down **c**: dotted lines indicate hydrogen bonds.

Table 2. *Hydrogen-bond distances and angles*

Symmetry code: none, *x*,*y*,*z*; (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $\bar{x},\bar{y},\bar{z}$; (iv) $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$. The atoms with superscripts $y-1$, $z-1$ are in the adjacent cell.

N(1)···O(4^{iii})	2·80 Å	C(1)–N(1)–O(4^{iii})$^{z-1}$	111·8°
N(1)···O(3)$^{y-1}$	2·75	C(1)–N(1)–O(3)$^{y-1}$	116·6
N(1)···O(2^{ii})$^{z-1}$	2·74	C(1)–N(1)–O(2^{ii})$^{z-1}$	111·5
N(2)···O(1^{ii})	3·06	C(2)–N(2)–O(1^{ii})	107·2
		C(3)–N(2)–O(1^{ii})	118·9
N(3)···O(4^{ii})	3·12	C(4)–N(3)–O(4^{ii})	102·8
		C(5)–N(3)–O(4^{ii})	138·8

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32375 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Bond distances* (Å) *and angles* (°)

E.s.d.'s are 0·015–0·03 Å and 1·0–2·5°.

N(1)–C(1)	1·52	N(3)–C(5)	1·50
C(1)–C(2)	1·59	C(5)–C(6)	1·55
C(2)–O(1)	1·21	C(6)–O(3)	1·24
C(2)–N(2)	1·35	C(6)–O(4)	1·26
N(2)–C(3)	1·51	C(1)–C(7)	1·61
C(3)–C(4)	1·54	C(7)–C(8)	1·62
C(4)–O(2)	1·22	C(8)–C(9)	1·58
C(4)–N(3)	1·36	C(8)–C(10)	1·47
N(1)–C(1)–C(2)	106·5	N(3)–C(5)–C(6)	110·9
C(1)–C(2)–O(1)	123·1	C(5)–C(6)–O(3)	120·7
C(1)–C(2)–N(2)	110·7	C(5)–C(6)–O(4)	113·4
O(1)–C(2)–N(2)	125·4	O(3)–C(6)–O(4)	125·7
C(2)–N(2)–C(3)	118·8	N(1)–C(1)–C(7)	114·6
N(2)–C(3)–C(4)	105·8	C(1)–C(7)–C(8)	109·2
C(3)–C(4)–O(2)	121·3	C(7)–C(8)–C(9)	103·2
C(3)–C(4)–N(3)	114·8	C(7)–C(8)–C(10)	116·6
O(2)–C(4)–N(3)	124·1	C(9)–C(8)–C(10)	119·4
C(4)–N(3)–C(5)	114·6		

Table 4. *The deviations of the atoms from the least-squares planes* (Å)

The equation of the plane is $ax + by + cz + d = 0$.

(i) Peptide group

C(1)	0·050	$a = 0·929$
C(2)	−0·068	$b = -0·121$
O(1)	0·014	$c = 0·349$
N(2)	−0·040	$d = -3·122$
C(3)	0·043	
C(3)	0·010	$a = 0·980$
C(4)	0·000	$b = -0·165$
O(2)	−0·006	$c = 0·109$
N(3)	−0·016	$d = -2·505$
C(5)	0·015	

(ii) Carboxyl group

C(5)	0·003	$a = 0·992$
C(6)	−0·005	$b = 0·047$
O(3)	0·004	$c = -0·117$
O(4)	0·004	$d = -3·356$

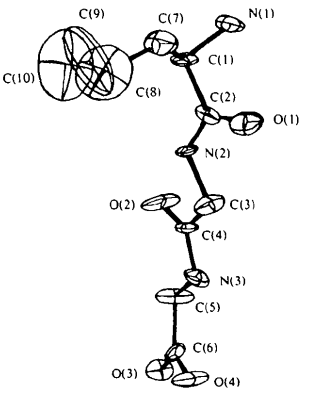

Fig. 2. Perspective view of the molecule.

general these values are close to those expected. There are, however, some relatively large deviations especially at the leucyl end, but the thermal motion is also large for these atoms. The dimensions of the carboxyl group suggest that the molecule is a zwitterion.

Least-squares planes (Table 4) show that the two peptide groups and the carboxyl group are effectively planar. As in glycylglycine nitrate (Narasinga Rao & Parthasarathy, 1973) the peptide plane and the plane of the carboxyl group are found to be nearly parallel (17·8°).

A perspective drawing of the molecule (Johnson, 1965) is shown in Fig. 2. The pertinent torsion angles of the peptide are given in Table 5, following the nomenclature of the IUPAC–IUB Commission on Biochemical Nomenclature (1971). The backbone chain conformation around C_α is given by $\varphi_2 = -167·5$, $\psi_{21} = -172·3$, $\varphi_3 = -164·8$, $\psi_7^2 = -177·4°$. The comparison of these values with $\varphi = 180°$ and $\psi = 180°$ for a fully extended chain shows that the molecule is almost in an extended conformation. The values for ω_1, 171·3°, and ω_2, −178·2°, indicate that the peptide is twisted significantly and is in the *trans* configuration. The side chain of the leucyl residue is characterized by three torsion angles χ_1, χ_{21} and χ_{22} and these angles can have values around 60, 180 or 300°. In the present molecule these angles are 171·2, 171·7 and 308·8°. The corresponding values found in other peptides are 294, 155, and 272° in leucylglycine HBr (Rao, 1969), 279, 170 and 292° in leucylprolylglycine (Leung & Marsh, 1958), 181, 63 and 185° in *N*-methyl-DL-leucylglycine HBr (Chandrasekharan & Subramanian, 1969) and 167, 74 and −162° in DL-leucylglycine ethyl ester (Timmins, 1975). It is interesting to note that the χ values for Lgg are near 180, 180, 300° whereas the corresponding angles in the other peptides are close to either 300, 180, 300° or 180, 60, 180°.

Table 5. *Torsion angles*

Bond	Atoms	Designation	Angles (°)
C_α–C′	N(1)–C(1)–C(2)–N(2)	ψ_{11}	−129·3
	–O(1)	ψ_{12}	48·9
C′–N	C(1)–C(2) N(2) C(3)	ω_1	171·3
N–C_α	C(2)–N(2)–C(3)–C(4)	φ_2	−167·5
C_α–C′	N(2)–C(3)–C(4)–N(3)	ψ_{21}	−172·3
	–O(2)	ψ_{22}	6·8
C′–N	C(3)–C(4)–N(3)–C(5)	ω_2	−178·2
N–C_α	C(4)–N(3)–C(5)–C(6)	φ_3	−164·8
C_α–C′	N(3)–C(5)–C(6)–O(3)	ψ_7^1	0·7
	–O(4)	ψ_7^2	−177·4
C_α–C_β	N(1)–C(1)–C(7)–C(8)	χ_1	171·2
C_β–C_γ	C(1)–C(7)–C(8)–C(9)	χ_{21}	171·7
	–C(10)	χ_{22}	−51·2
C_α–C′	C(2)–C(1)–C(7)–C(8)		−72·8
C′–N	O(1)–C(2)–N(2)–C(3)		3·6
C′–N	O(2)–C(4)–N(3)–C(5)		2·7

Our thanks are due to H. Rajagopal for computational help.

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10-Hydroxy-3-methoxy-2,4a-ethano-5,8-methanoperhydronaphthalene: An Example of Steric Preference in Photochemical Addition*

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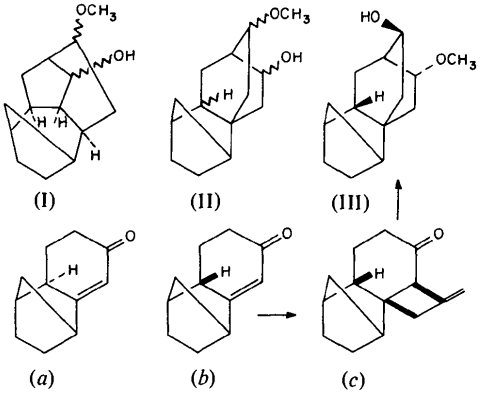
(*Received* 30 *November* 1976; *accepted* 17 *December* 1976)

Abstract. $C_{14}H_{22}O_2$, monoclinic, $C2/c$, $a = 11{\cdot}821\ (2)$, $b = 6{\cdot}435\ (2)$, $c = 31{\cdot}567\ (2)$ Å, $\beta = 92{\cdot}24\ (2)°$, $V = 2399{\cdot}4$ Å^3, $Z = 8$, $D_x = 1{\cdot}231$, $D_m = 1{\cdot}239$ g cm^{-3} (flotation in KI solution at 22 °C). The structure has been determined by X-ray analysis, and its synthesis has been found to conform to the photoaddition rule. The direct method was used and block-diagonal least-squares refinement led to $R = 0{\cdot}042$, $R_w = 0{\cdot}039$ for the 1759 observed reflexions. The molecules are interlinked by hydrogen bonds to form separate continuous chains.

Introduction. $C_{14}H_{22}O_2$ was synthesized by K. Wiesner and his collaborators by a method that they wished to utilize in the synthesis of delphinium alkaloids. The method was based on the re-arrangement postulated for the biogenesis of this type of skeleton (Valenta & Wiesner, 1956), and the product was predicted to be (I). Further chemical studies, however, ascertained that the compound had failed to re-arrange as predicted and (II) was then proposed. The actual structure found by this analysis was (III).



Determination of the stereochemistry of the compound was needed in order to clarify the steric preference of the photochemical addition by which the system was constructed. From this work, Wiesner (1973) concluded that the starting material was (*b*) rather than (*a*), (*b*) being converted with complete stereospecificity into the allene photoadduct (*c*). The conversion of (*c*) to (III) had been accomplished by standard methods which left no doubt that the methoxy group in (III) was derived from the ketone function in (*c*).

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