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Structures of Two *N*-Boc Amino-Acid Phenacyl Esters

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Abstract. (I): *tert*-Butoxycarbonyl-L-phenylalanine phenacyl ester, $C_{22}H_{25}NO_5$, M_r = 383·4, orthorhombic, $P2_12_12_1$, a = 9·277 (3), b = 14·379 (3), c = 15·874 (3) Å, V = 2117·5 (5) Å^3, Z = 4, D_x = 1·203 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·80 cm^{-1}, F(000) = 816, room temperature, final R = 0·033 for 893 observed reflections. (II): *tert*-Butoxycarbonylglycine phenacyl ester, $C_{15}H_{19}NO_5$, M_r = 293·3, monoclinic, $P2_1/n$, a = 5·105 (2), b = 26·593 (3), c = 11·406 (2) Å, β = 90·91 (3)°, V = 1548·3 (5) Å^3, Z = 4, D_x = 1·259 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·90 cm^{-1}, F(000) = 624, room temperature, final R = 0·0438 for 1016 observed reflections. The values of bond lengths and angles of the Boc group and the urethane moiety, as well as the distances of the phenacyl and ester CO are normal. The urethane amide bonds [O(5)—C(6)—N(8)—C(9) = 174·4 (2)° in (I); −178·4 (2)° in (II)] have the *trans* conformation in both compounds. In (I) and (II) the molecules are interconnected by intermolecular hydrogen bonds of different types [O(22)···H(8) = 2·207 (75) Å in (I); O(7)···H(8) = 2·114 (65) Å in (II)]. As a result of the *trans* conformation adopted by the amide bond of the urethane moiety in both molecules, O(5) and H(8) are forced to have short non-bonded contacts [O(5)—H(8) = 2·308 (77) Å in (I); 2·250 (64) Å in (II)].

Introduction. We recently reported a simple method for isolating free amino acids as their *N*-Boc (*N-tert*-butoxycarbonyl) amino-acid benzyl esters from marine organisms (Matsoukas, Moharir & Findlay, 1983; Findlay, Daljeet, Matsoukas & Moharir, 1984). One limitation of this method is the oily nature of the non-polar amino-acid derivatives. In order to improve this method we have synthesized the phenacyl esters (Stelakatos, Panagou & Zervas, 1966) of several *N*-Boc amino acids which crystallize easily. This procedure was applied to isolate major free amino acids from the Mediterranean fruit fly *Ceratitis capitata*. The crystal structure determinations of the title compounds were undertaken to establish the conformation adopted by peptide molecules. Furthermore, we were interested in the position and the role of the phenacyl CO, in the *cis–trans* isomerism around the urethane —O(O=)C—NH— bond, and in information concerning possibly important non-bonded interactions.

Experimental. (I). Pure *N*-Boc-L-phenylalanine was prepared by the method of Nagasawa, Kuroiwa, Narita & Isowa (1973). Esterification was achieved, without racemization, with phenacyl bromide–triethylamine (Stelakatos, Panagou & Zervas, 1966). Recrystallization from ethyl acetate–petroleum ether, m.p. = 398 K. Prismatic crystal 0·22 × 0·28 × 0·72 mm with prominent axis [$\bar{1}$00]. Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters determined from 50 reflections (8 < θ < 12°), $\omega/2\theta$ scan technique up to 2θ = 54°, scan width (0·8 + 0·3 tanθ)°, scan rate 1·27–16·48° min^{-1}, background 1/4 of the scan time at each scan limit, max. scan time 60 s, aperture (2·4 + 0·9 tanθ) mm. 5198 measured reflections, 2628

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Table 1. *Final positional* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Compound (I)				
C(1)	6023 (7)	1210 (3)	5321 (4)	4·70
C(2)	7516 (7)	1650 (4)	5324 (6)	8·19
C(3)	5268 (9)	1410 (4)	4508 (5)	7·66
C(4)	5170 (9)	1511 (5)	6079 (5)	7·95
O(5)	6366 (4)	211 (2)	5375 (3)	4·67
C(6)	5319 (6)	−430 (4)	5398 (3)	3·69
O(7)	4027 (4)	−274 (3)	5327 (3)	5·32
N(8)	5893 (5)	−1273 (3)	5516 (3)	3·28
C(9)	5053 (6)	−2104 (3)	5643 (3)	3·14
C(10)	5136 (7)	−2455 (3)	6563 (3)	4·31
C(11)	4595 (6)	−1742 (4)	7178 (3)	3·81
C(12)	5511 (8)	−1141 (4)	7579 (4)	5·79
C(13)	5014 (10)	−465 (5)	8136 (4)	7·22
C(14)	3572 (11)	−396 (6)	8294 (5)	7·84
C(15)	2637 (9)	−998 (7)	7902 (5)	8·13
C(16)	3125 (7)	−1670 (5)	7347 (4)	5·58
C(17)	5589 (6)	−2851 (3)	5038 (4)	3·16
O(18)	6505 (4)	−2752 (3)	4519 (3)	4·57
O(19)	4908 (4)	−3663 (2)	5179 (2)	4·22
C(20)	5379 (6)	−4434 (3)	4661 (4)	4·07
C(21)	4671 (6)	−4435 (4)	3811 (3)	3·36
H(8)	6828 (80)	−1337 (49)	5646 (43)	9·61
Compound (II)				
C(1)	6656 (8)	2502 (2)	6367 (5)	4·97
C(2)	4976 (9)	2717 (2)	5398 (4)	5·70
C(3)	8476 (10)	2104 (2)	5887 (6)	7·94
C(4)	5105 (10)	2299 (2)	7385 (5)	6·31
O(5)	8517 (5)	2889 (1)	6817 (3)	5·52
C(6)	7666 (8)	3316 (2)	7280 (4)	4·04
O(7)	5385 (5)	3431 (1)	7431 (3)	4·52
N(8)	9687 (7)	3620 (1)	7551 (3)	4·29
C(9)	9139 (8)	4100 (2)	8098 (4)	3·94
C(10)	7826 (8)	4034 (2)	9266 (4)	3·67
O(11)	8351 (6)	3719 (1)	9979 (3)	5·13
O(12)	5988 (5)	4390 (1)	9421 (2)	3·76
C(13)	4684 (8)	4361 (2)	10517 (4)	3·86
C(14)	6435 (9)	4531 (2)	11515 (4)	4·24
O(15)	8452 (7)	4761 (1)	11319 (3)	5·50
C(16)	5677 (10)	4408 (2)	12732 (4)	4·80
C(17)	3576 (13)	4110 (2)	12968 (5)	7·44
C(18)	3021 (17)	3985 (3)	14136 (8)	9·60
C(19)	4528 (19)	4158 (3)	15018 (7)	9·73
C(20)	6591 (20)	4462 (4)	14775 (7)	12·58
C(21)	7172 (14)	4586 (3)	13646 (6)	9·01
H(8)	11261 (117)	3486 (23)	7507 (48)	9·69

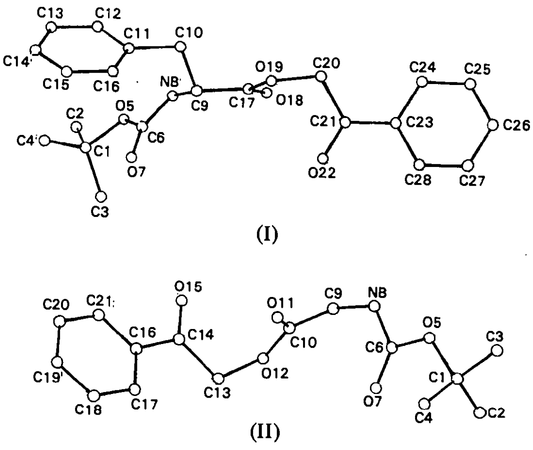
averaged, mean discrepancy on I 1·7% for 5052 reflections, 893 observed with $I > 2{\cdot}5\sigma(I)$. $0 \le h \le 10$, $0 \le k \le 17$, $0 \le l \le 16$, reference reflections ($\bar{1}3\bar{3}$, $\bar{2}30$, $\bar{3}50$), orientation control reflections ($\bar{2}2\bar{5}$, $\bar{1}4\bar{5}$, $\bar{1}45$), no significant variation during data collection. $R = 0{\cdot}033$ for 893 reflections, $wR = 0{\cdot}0327$, $\sum w(\Delta F)^2$ minimized, $w = k/[\sigma^2(F) + 0{\cdot}01103F^2]$, max. Δ/σ [for N(8)] = 0·20, max. and min. electron densities in final difference map 0·10 and −0·17 e Å^{-3}. All non-H atoms refined with anisotropic thermal parameters, and all H atoms were placed in geometrically calculated positions, riding model, except H(8) which was located by a difference Fourier synthesis and refined isotropically.

(II). This compound was prepared by the same procedure, m.p. = 333–334 K. Prismatic crystal 0·24 × 0·25 × 0·78 mm, prominent axis [100]. Enraf–Nonius CAD-4, Mo $K\alpha$, 50 reflections for lattice parameters ($7 < \theta < 11°$), $\omega/2\theta$ scan up to $2\theta \le 54°$. 6989 measured reflections, 3474 averaged, mean discrepancy on I 2·4% for 6868 reflections, 1016 observed with $I > 2{\cdot}5\sigma(I)$. Reference reflections (044, 172, 190), orientation control reflections (083, 144, 16$\bar{4}$), intensity decrease −0·6% $-6 \le h \le 6$, $0 \le k \le 29$, $0 \le l \le 12$. $R = 0{\cdot}0438$ for 1016 observed reflections, $wR = 0{\cdot}0462$, $\sum w(\Delta F)^2$ minimized, $w = k/[\sigma^2(F) + 0{\cdot}01036F^2]$, max. Δ/σ [for N(8)] = 0·43, max. and min. electron densities in final difference map 0·18 and −0·23 e Å^{-3}. All non-H atoms refined anisotropically, and H atoms calculated except H(8) which was located and refined with isotropic temperature factors.

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

Compound (I)		Compound (II)	
C(1)—C(2)	1·523 (8)	C(1)—C(2)	1·502 (6)
C(1)—C(3)	1·496 (8)	C(1)—C(3)	1·516 (6)
C(1)—C(4)	1·504 (9)	C(1)—C(4)	1·516 (7)
C(1)—O(5)	1·473 (6)	C(1)—O(5)	1·488 (5)
O(5)—C(6)	1·340 (6)	O(5)—C(6)	1·327 (5)
C(6)—O(7)	1·224 (6)	C(6)—O(7)	1·219 (4)
C(6)—N(8)	1·338 (7)	C(6)—N(8)	1·344 (5)
N(8)—H(8)	0·897 (72)	N(8)—H(8)	0·881 (60)
C(17)—O(18)	1·192 (6)	C(10)—O(11)	1·194 (5)
C(21)—O(22)	1·225 (6)	C(14)—O(15)	1·222 (5)
C(2)—C(1)—C(3)	110·4 (6)	C(2)—C(1)—C(3)	110·2 (5)
C(2)—C(1)—C(4)	110·8 (6)	C(2)—C(1)—C(4)	113·6 (4)
C(2)—C(1)—O(5)	102·0 (5)	C(2)—C(1)—O(5)	110·1 (4)
C(13)—C(1)—C(4)	112·9 (6)	C(3)—C(1)—C(4)	111·0 (5)
C(3)—C(1)—O(5)	109·9 (5)	C(3)—C(1)—O(5)	102·5 (3)
C(4)—C(1)—O(5)	110·3 (5)	C(4)—C(1)—O(5)	108·7 (4)
C(1)—O(5)—C(6)	121·0 (4)	C(1)—O(5)—C(6)	121·2 (3)
O(5)—C(6)—O(7)	125·6 (5)	O(5)—C(6)—O(7)	126·3 (4)
O(5)—C(6)—N(8)	109·8 (4)	O(5)—C(6)—N(8)	110·5 (3)
O(7)—C(6)—N(8)	124·6 (5)	O(7)—C(6)—N(8)	123·2 (4)
C(6)—N(8)—C(9)	123·8 (4)	C(6)—N(8)—C(9)	118·4 (3)
C(6)—N(8)—H(8)	120·7 (46)	C(6)—N(8)—H(8)	116·1 (39)
C(9)—N(8)—H(8)	114·0 (46)	C(9)—N(8)—H(8)	124·3 (38)
O(5)—C(6)—N(8)—C(9)	174·41 (10)	O(5)—C(6)—N(8)—C(9)	−178·39 (20)
C(6)—N(8)—C(9)—C(10)	−108·04 (16)		
C(6)—N(8)—C(9)—C(17)	129·67 (18)		
C(10)—C(9)—C(17)—O(19)	52·04 (15)		
O(22)···H(8$^{\rm i}$)	2·207 (75)	O(7)···H(8$^{\rm ii}$)	2·114 (65)

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



(II)

Fig. 1. Molecular structures of compounds (I) and (II) with numbering of the atoms.

For (I) and (II), intensities corrected for Lp; absorption corrections and secondary extinction not used; atomic scattering factors from *SHELX*76. Structures solved by direct methods with *MULTAN*11/84 (Main, Germain & Woolfson, 1984), *SHELX*76 (Sheldrick, 1976), *SHELXS*86 (Sheldrick, 1986) and *PLUTO* (Motherwell & Clegg, 1978).

Discussion. The refined atomic coordinates and isotropic temperature factors are presented in Table 1;* important bond distances and bond angles are given in Table 2; the molecular structures and the numbering of the atoms are shown in Fig. 1. The observed values of bond lengths and bond angles of the Boc group and urethane moiety are normal (Table 2). The bond lengths of the phenacyl C=O in both molecules are similar [C(21)—O(22) = 1·225 (6) Å (I); C(14)—O(15) = 1·222 (5) Å (II)]. The ester C=O distances are slightly shorter [C(17)—O(18) = 1·192 (6) Å (I); C(10)—O(11) = 1·194 (5) Å (II)]. This small difference between phenacyl and ester C=O might be a result of the resonance effect of the phenyl ring. The urethane amide bond adopts the *trans* conformation for the two compounds with O(5)—C(6)—N(8)—C(9) torsion angles of 174·4 (2) and −178·4 (2)° respectively. The difference of dihedral angles might be due to the presence of the phenylalanine side chain. In compound (I) the urethane N—H forms an intermolecular hydrogen bond with the phenacyl C=O of a neighbouring molecule [O(22)···H(8) = 2·207 (75) Å]. In compound (II) the crystals are stabilized by intermolecular bonds involving the urethane moieties [O(7)···H(8) = 2·114 (65) Å]. The preference of the phenacyl and urethane C=O to participate in hydrogen bonding indicates that they are better hydrogen-bond acceptors than the ester C=O group.

The *trans* amide linkage in the urethane moiety of both compounds places O(5) and H(8) in a *cis* arrangement with O(5)—H(8) = 2·308 (77) Å in (I) and 2·250 (64) Å in (II).

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44164 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 2,3-Dibenzoyl-1-methylbicyclo[2.2.2]octa-2,5-diene

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Abstract. $C_{23}H_{20}O_2$, $M_r = 328·41$, monoclinic, $P2_1$, $a = 5·890$ (1), $b = 13·910$ (2), $c = 10·722$ (2) Å, $\beta = 101·01$ (2)°, $V = 862·27$ Å^3, $Z = 2$, $F(000) = 348$, D_m(by flotation) = 1·257, $D_x = 1·265$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·7107$ Å, $\mu = 0·856$ cm^{-1}, $R = 0·036$ for 1232 reflections with $I > 2\sigma(I)$. This structural study was aimed primarily at determining the conformation of the carbonyl groups. The structure could not be solved by a usual direct-methods program and a random phasing approach proved successful. Besides