64. *N*-Acylureas in Peptide Synthesis: An X-Ray Diffraction and IR-Absorption Study

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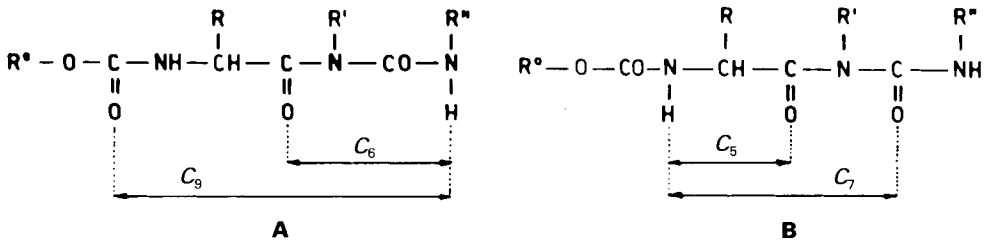
An X-ray diffraction analysis of two *N*-acyl derivatives of symmetrical dialkylureas, *N*-[N^{α}-(benzyloxycarbonyl)-L-valyl]-*N,N'*-diisopropylurea (**1**) and *N*-{N^{α}-[(*tert*-butyloxy)carbonyl]-L-valyl}-*N,N'*-dicyclohexylurea (**2**), and one *N*-acyl derivative of an unsymmetrical *N,N'*-dialkylurea, *N*-[N^{α}-(benzyloxycarbonyl)-L-valyl]-*N'*-(*tert*-butyl)-*N*-ethylurea (**3**), has been performed. It was established that it is the least hindered *O*-acylisourea N-atom that attacks intramolecularly the carbonyl group of the N^{α}-protected amino acid activated by the unsymmetrical carbodiimide to form the major rearrangement product. The occurrence and nature of intra- and intermolecularly H-bonded forms of the *N*-acylureas in the crystal state were also assessed. It was also shown that soluble *N*-acylureas may compete with intermolecular (peptide)N–H···O=C(peptide) H-bonds in CH_2Cl_2.

Introduction. – The formation of *N*-acylurea is the most commonly encountered side reaction in the activation of carboxyl group by carbodiimides [1]. The isolation of these side products has already been reported in early papers on application of *N,N'*-dicyclohexylcarbodiimide (DCC) [2–7]. Systematic investigations carried out in the *Warsaw* laboratory [8] [9] revealed that N^{α}-protected (*tert*-butyloxy)carbonyl- and benzyloxycarbonyl-amino acids, activated with DCC in CH_2Cl_2, form from 2 to 12% of *N*-acylurea depending upon the nature of the amino acid and the protecting group. A significant increase in *N*-acylurea formation was observed when the coupling was carried out in tetrahydrofuran or *N,N'*-dimethylformamide. The same side reaction was also noted in the coupling mediated by *N,N'*-diisopropylcarbodiimide [10].

In the course of our search for carbodiimides, which retain the efficiency of DCC but yield ureas soluble in CH_2Cl_2, we examined several carbodiimides both symmetrically and unsymmetrically substituted [11–13]. In all cases, some *N*-acylurea formation was observed. The amount of the side product depends on the nature of the substituents. In the cases of unsymmetrically substituted carbodiimides, two *N*-acylureas are formed. The determination of the structure of *N*-acylureas is essential to recognize the direction to be followed in the development of new carbodiimides which are less likely to cause this side reaction.

The aim of the present study is twofold: to establish the structure of *N*-acylureas, including an example of a compound derived from an unsymmetrical carbodiimide, and

to contribute to our continuing research on the relationship between conformation and self-association of [C(=O)–NH]-containing compounds and their solubility [14–23]. We describe here results of an X-ray diffraction study of single crystals of two *N*-acylureas derived from symmetrical carbodiimides, *N*-[N^{α}-(benzyloxycarbonyl)-L-valyl]-*N*,*N*′-diisopropylurea (**1**) and *N*-{N^{α}-[(*tert*-butyloxy)carbonyl]-L-valyl}-*N*,*N*′-dicyclohexylurea (**2**), and one *N*-acylurea derived from an unsymmetrical carbodiimide, *N*-[N^{α}-(benzyloxycarbonyl)-L-valyl]-*N*′-(*tert*-butyl)-*N*-ethylurea (**3**). The major objective of this analysis was to determine the nature and extent of the intra- and intermolecularly H-bonded forms adopted by *N*,*N*′-dialkylureas monoacylated by an N^{α}-protected amino-acid residue. The possible types of intramolecularly H-bonded forms in the *N*-[(acylamino)acyl]urea system –CO–NH–CH(R)–CO–N(R′)–CO–NH(R″) investigated in this work are illustrated by *Formula* **A** showing the six- and nine-membered ring forms with the *ureide* NH group acting as the H-bonding donor and *Formula* **B** showing the five- and seven-membered ring forms with the *urethane* NH group as the H-bonding donor.



1 R = R′ = R″ = i-Pr, R° = $PhCH_2$
2 R = i-Pr, R′ = R″ = cyclohexyl, R° = *t*-Bu
3 R = i-Pr, R′ = Et, R″ = *t*-Bu, R° = $PhCH_2$

In view of their practical interest, particularly to solid-phase peptide synthesis [24–32], the IR-absorption results obtained upon addition of the CH_2Cl_2-soluble *N*-acylurea **1** to a self-associated peptide are also reported. They are compared to those already published [14] for ureines.

X-Ray Diffraction Analysis of *N*-Acylureas. – The molecular structures of *N*-acylureas **1**–**3** are illustrated in *Figs. 1–3*. Torsion angles are listed in the *Table*.

A dramatic conformational difference between the two *N*-acylureas **1** and **3** is seen in the imide C(14)–N(2)–C(13)–C(9) torsion angle, *cis* (– 5.9(10)°) in **1** but *trans* (179.7(6)°) in **3**. The major consequence of this structural difference is the intramolecularly H-bonded C_9 form for **1** and the C_6 form for **3**; the latter has been reported for several *N*-acylureas [33–37]. While the N(3)···O(2) intramolecular separation in the C_9 form of **1** (2.864(10) Å) is in the expected range [38] [39], the N(3)···O(3) intramolecular separation in the C_6 form of **3** is very short (2.575(10) Å). The N(3)H···O(2) and N(3)H···O(3) distances in **1** and **3** are 1.845(15) and 1.698(15) Å, respectively. Conversely, the amide C(7)–N(2)–C(14)–C(15) torsion angle of **2** (– 19.3(26)°) indicates a distorted *cis*-conformation [40] [41]. No evidence for intramolecular N–H···O=C H-bonds of the C_5 type nor of the C_7 type has been observed in any of the three *N*-acylureas.

Table. *Torsion Angles* [°] *for* N-[N$^{\alpha}$-(*Benzyloxycarbonyl*)-L-*valyl*]-N,N′-*diisopropylurea* (**1**), N-{N$^{\alpha}$-[(tert-*Butyloxy*)*carbonyl*]-L-*valyl*}-N,N′-*dicyclohexylurea* (**2**), *and* N-[N$^{\alpha}$-(*Benzyloxycarbonyl*)-L-*valyl*]-N-(tert-*butyl*)-N-*ethylurea* (**3**). Arbitrary numbering.

1		**2**		**3**	
C(7)–O(1)–C(8)–O(2)	5.9(11)	C(20)–O(4)–C(19)–O(3)	– 9.0(30)	C(7)–O(1)–C(8)–O(2)	– 1.7(12)
C(7)–O(1)–C(8)–N(1)	– 174.9(6)	C(19)–O(4)–C(20)–C(21)	– 176.8(17)	C(7)–O(1)–C(8)–N(1)	179.2(7)
C(8)–O(1)–C(7)–C(6)	– 89.0(8)	C(19)–O(4)–C(20)–C(22)	– 56.0(25)	C(8)–O(1)–C(7)–C(6)	– 109.4(8)
C(9)–N(1)–C(8)–O(2)	– 5.2(11)	C(19)–O(4)–C(20)–C(23)	80.3(23)	C(9)–N(1)–C(8)–O(2)	– 9.3(12)
C(9)–N(1)–C(8)–O(1)	175.6(6)	C(20)–O(4)–C(19)–N(3)	175.6(15)	C(9)–N(1)–C(8)–O(1)	169.7(6)
C(8)–N(1)–C(9)–C(10)	– 178.4(7)	C(1)–N(1)–C(7)–O(2)	– 7.9(27)	C(8)–N(1)–C(9)–C(10)	161.6(7)
C(8)–N(1)–C(9)–C(13)	– 58.3(8)	C(1)–N(1)–C(7)–N(2)	179.0(14)	C(8)–N(1)–C(9)–C(13)	– 78.0(8)
C(13)–N(2)–C(14)–O(4)	126.1(8)	C(7)–N(1)–C(1)–C(6)	108.1(19)	C(13)–N(2)–C(14)–O(4)	– 178.6(7)
C(14)–N(2)–C(13)–O(3)	178.5(7)	C(7)–N(1)–C(1)–C(2)	– 128.7(18)	C(14)–N(2)–C(13)–O(3)	2.3(11)
C(18)–N(2)–C(13)–O(3)	– 3.7(10)	C(8)–N(2)–C(14)–O(1)	0.9(26)	C(19)–N(2)–C(13)–O(3)	176.9(7)
C(18)–N(2)–C(14)–O(4)	– 51.7(10)	C(7)–N(2)–C(14)–O(1)	162.0(16)	C(19)–N(2)–C(14)–O(4)	6.4(9)
C(14)–N(2)–C(18)–C(19)	89.7(9)	C(8)–N(2)–C(7)–N(1)	– 95.3(17)	C(14)–N(2)–C(19)–C(20)	80.8(8)
C(13)–N(2)–C(18)–C(19)	– 88.3(9)	C(8)–N(2)–C(7)–O(2)	91.1(19)	C(13)–N(2)–C(19)–C(20)	– 94.4(8)
C(14)–N(2)–C(18)–C(20)	– 44.4(10)	C(14)–N(2)–C(7)–N(1)	102.9(19)	C(19)–N(2)–C(14)–N(3)	– 175.8(6)
C(13)–N(2)–C(18)–C(20)	137.7(8)	C(14)–N(2)–C(7)–O(2)	– 70.7(22)	C(13)–N(2)–C(14)–N(3)	– 0.8(10)
C(18)–N(2)–C(14)–N(3)	125.7(7)	C(8)–N(2)–C(14)–C(15)	179.5(16)	C(19)–N(2)–C(13)–C(9)	– 5.6(9)
C(13)–N(2)–C(14)–N(3)	– 56.5(0)	C(7)–N(2)–C(14)–C(15)	– 19.3(26)	C(14)–N(2)–C(13)–C(9)	179.7(6)
C(18)–N(2)–C(13)–C(9)	171.9(7)	C(7)–N(2)–C(8)–C(9)	104.9(21)	C(15)–N(3)–C(14)–N(2)	177.0(6)
C(14)–N(2)–C(13)–C(9)	– 5.9(10)	C(7)–N(2)–C(8)–C(13)	– 9.1(22)	C(15)–N(3)–C(14)–O(4)	– 5.3(12)
C(15)–N(3)–C(14)–N(2)	168.5(6)	C(14)–N(2)–C(8)–C(13)	153.1(19)	C(14)–N(3)–C(15)–C(16)	– 63.1(10)
C(15)–N(3)–C(14)–O(4)	– 14.4(12)	C(14)–N(2)–C(8)–C(9)	– 92.9(23)	C(14)–N(3)–C(15)–C(17)	62.4(10)
C(14)–N(3)–C(15)–C(16)	162.9(7)	C(15)–N(3)–C(19)–O(3)	0.3(30)	C(14)–N(3)–C(15)–C(18)	– 179.7(7)
C(14)–N(3)–C(15)–C(17)	– 72.9(9)	C(15)–N(3)–C(19)–O(4)	175.9(18)	C(2)–C(1)–C(6)–C(7)	175.7(7)

C(2)–C(1)–C(6)–C(7)	176.1(6)	C(19)–N(3)–C(15)–C(14)	– 136.1(18)	C(2)–C(1)–C(6)–C(5)	0.0(8)
C(2)–C(1)–C(6)–C(5)	0.0(8)	C(19)–N(3)–C(15)–C(16)	103.9(21)	C(6)–C(1)–C(2)–C(3)	0.1(8)
C(6)–C(1)–C(2)–C(3)	– 0.1(8)	N(1)–C(1)–C(6)–C(5)	– 173.6(17)	C(1)–C(2)–C(3)–C(4)	– 0.1(8)
C(1)–C(2)–C(3)–C(4)	0.1(8)	N(1)–C(1)–C(2)–C(3)	– 179.2(17)	C(2)–C(3)–C(4)–C(5)	0.0(8)
C(2)–C(3)–C(4)–C(5)	0.0(8)	C(2)–C(1)–C(6)–C(5)	61.4(24)	C(3)–C(4)–C(5)–C(6)	0.0(8)
C(3)–C(4)–C(5)–C(6)	– 0.1(8)	C(6)–C(1)–C(2)–C(3)	– 56.2(24)	C(4)–C(5)–C(6)–C(1)	0.0(8)
C(4)–C(5)–C(6)–C(1)	0.1(8)	C(1)–C(2)–C(3)–C(4)	58.3(26)	C(4)–C(5)–C(6)–C(7)	– 176.0(6)
C(4)–C(5)–C(6)–C(7)	– 176.3(8)	C(2)–C(3)–C(4)–C(5)	– 59.8(25)	C(1)–C(6)–C(7)–O(1)	– 80.1(9)
C(1)–C(6)–C(7)–O(1)	24.6(9)	C(3)–C(4)–C(5)–C(6)	62.7(24)	C(5)–C(6)–C(7)–O(1)	95.7(8)
C(5)–C(6)–C(7)–O(1)	– 159.3(6)	C(4)–C(5)–C(6)–C(1)	– 63.7(24)	N(1)–C(9)–C(13)–N(2)	156.6(6)
N(1)–C(9)–C(13)–N(2)	131.0(7)	N(2)–C(8)–C(13)–C(12)	– 180.0(20)	N(1)–C(9)–C(13)–O(3)	– 25.9(9)
N(1)–C(9)–C(13)–O(3)	– 53.3(9)	N(2)–C(8)–C(9)–C(10)	175.0(21)	C(10)–C(9)–C(13)–O(3)	96.2(8)
C(10)–C(9)–C(13)–O(3)	66.4(9)	C(9)–C(8)–C(13)–C(12)	64.4(28)	C(10)–C(9)–C(13)–N(2)	– 81.4(8)
C(10)–C(9)–C(13)–N(2)	– 109.3(7)	C(13)–C(8)–C(9)–C(10)	– 69.7(30)	N(1)–C(9)–C(10)–C(11)	61.7(8)
N(1)–C(9)–C(10)–C(11)	– 61.0(8)	C(8)–C(9)–C(10)–C(11)	62.3(31)	N(1)–C(9)–C(10)–C(12)	– 64.2(8)
N(1)–C(9)–C(10)–C(12)	176.5(7)	C(9)–C(10)–C(11)–C(12)	– 63.4(34)	C(13)–C(9)–C(10)–C(12)	175.4(7)
C(13)–C(9)–C(10)–C(12)	58.2(9)	C(10)–C(11)–C(12)–C(13)	66.6(34)	C(13)–C(9)–C(10)–C(11)	– 58.8(8)
C(13)–C(9)–C(10)–C(11)	– 179.3(6)	C(11)–C(12)–C(13)–C(8)	– 62.8(31)		
		O(1)–C(14)–C(15)–N(3)	– 27.5(26)		
		N(2)–C(14)–C(15)–N(3)	153.9(17)		
		N(2)–C(14)–C(15)–C(16)	– 83.9(22)		
		O(1)–C(14)–C(15)–C(16)	94.7(22)		
		C(14)–C(15)–C(16)–C(17)	176.3(18)		
		N(3)–C(15)–C(16)–C(17)	– 63.8(23)		
		C(14)–C(15)–C(16)–C(18)	– 60.7(23)		
		N(3)–C(15)–C(16)–C(18)	59.2(24)		

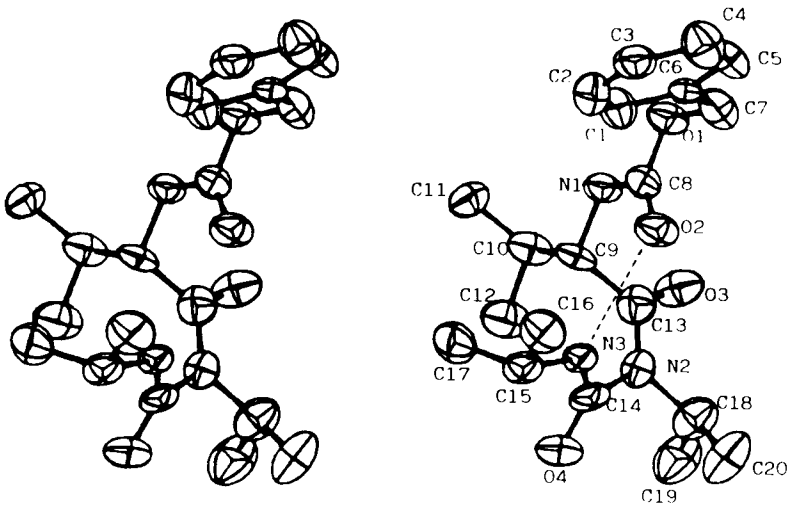


Fig. 1. *Stereoview of* N-[N^2-*(benzyloxycarbonyl)*-L-*valyl]*-N,N'-*diisopropylurea* (**1**). Thermal ellipsoids indicate 50% probability; arbitrary numbering.

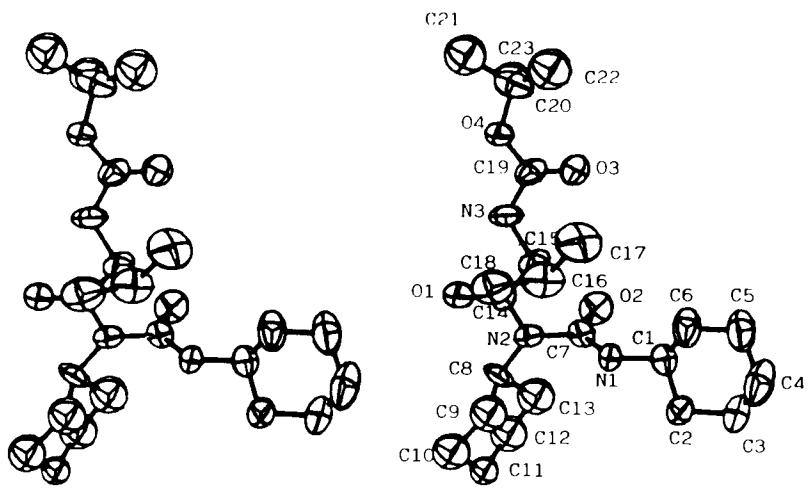
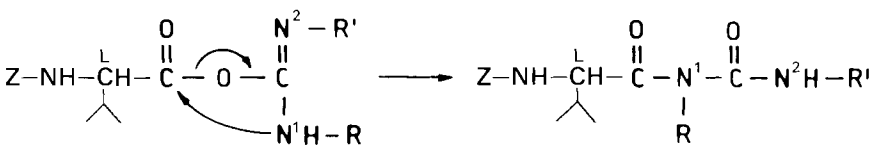


Fig. 2. *Stereoview of* N-[N^2-*(* tert-*butyloxycarbonyl)*-L-*valyl]*-N,N'-*dicyclohexylurea* (**2**). Thermal ellipsoids indicate 50% probability; arbitrary numbering.

Scheme



(R less hindered than R')

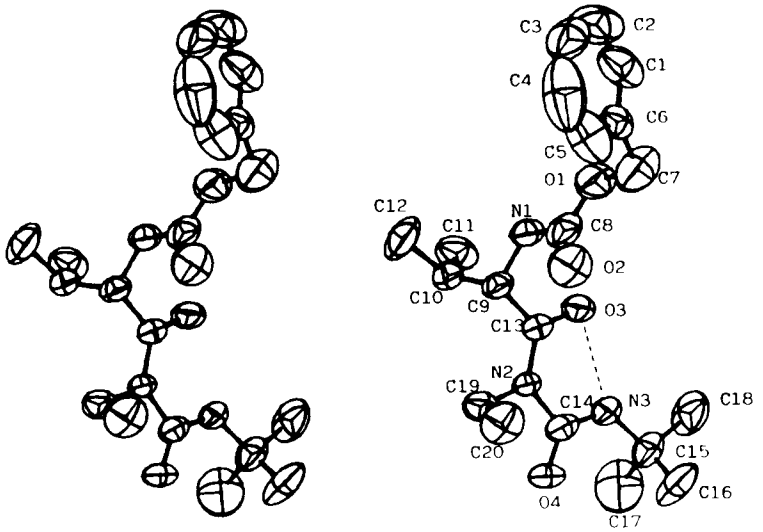


Fig. 3. *Stereoview of* N-[N$^{\alpha}$-(*benzyloxycarbonyl*)-L-*valyl*]-N′-(tert-*butyl*)-N-*ethylurea* (**3**). Thermal ellipsoids indicate 50% probability; arbitrary numbering.

It may be concluded that the *N*-[(acylamino)acyl]urea systems of compounds **1**–**3** assume three different dispositions in the crystal state: the intramolecularly H-bonded C_9 and C_6 forms in **1** and **3**, respectively, but an open form in **2**.

The crystallographic analysis of *N*-acylurea **3** has unequivocally established, *inter alia*, that it is the *least* hindered *O*-acylisourea N-atom N^1 that preferably attacks intramolecularly the carbonyl group of the N$^{\alpha}$-protected amino acid activated by the unsymmetrical carbodiimide, as depicted in the *Scheme* (4-center mechanism) [42].

IR-Absorption Analysis of Peptide/*N*-Acylurea Interactions. – A very useful probe to determine the onset of strong N–H···O=C H-bonds in peptides, as those typical of an intermolecular β-sheet structure and responsible for the low solubility of peptides in solvents of low polarity [14–23], is represented by the IR absorption band near 1630 cm^{-1} assigned to the C=O stretching mode [43–46].

Fig. 4 shows that this conformation is adopted by the model peptide Nps-Lys(Boc)-[Lys(Boc)]$_4$-Lys(Boc)-OChocb in CH_2Cl_2 solution (Nps = 2-nitrophenylsulfenyl, Boc = (*tert*-butyloxy)carbonyl, Chocb = 4-[(cholestan-3β-yloxy)carbonyl]benzyl). This peptide was synthesized in order to compare the solubility and self-association properties of peptides with cholestanyl ester C-terminal groups with those of the corresponding benzyl ester [17]. From *Fig. 4*, it is clear that upon addition of the soluble *N*-acylurea **1** to the strongly H-bonded peptide (peptide/*N*-acylurea molar ratio 1:10), the self-associated species are partially disrupted. Thus, we have been able to show that peptide/*N*-acylurea interactions may compete effectively with N–H···O=C peptide/peptide interactions. Interestingly, the effect exhibited by *N*-acylurea **1** in this process appears to be less powerful than that already reported [14] for *N*,*N*′-diisopropylurea characterized by the same alkyl moieties at the two N-atoms.

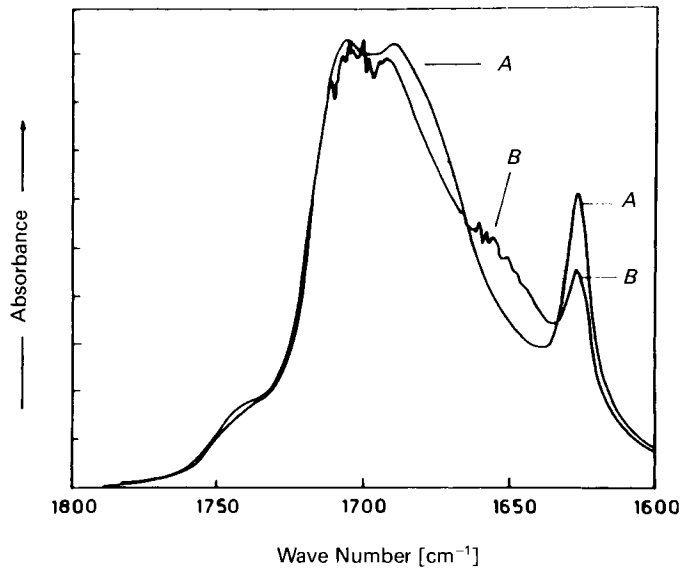


Fig. 4. *IR absorption spectra in the 1800–1600 cm^{-1} region of Nps-Lys(Boc)-[Lys(Boc)]$_4$-Lys(Boc)-OChocb in CH_2Cl_2 solution* (conc. $1.5 \cdot 10^{-2}$ M) *in the absence of* N-*acylurea* (*A*) *and in the presence of added* N-*acylurea* **1** (*B*). The peptide/*N*-acylurea molar ratio was 1:10, and the reference cuvette contained an appropriate solution of the *N*-acylurea in CH_2Cl_2.

Since in actual peptide synthesis only a small portion of the carboxyl component is converted to *N*-acylurea, the conclusion can be drawn that this side product should cause only a minor effect on the self-association properties of peptide chains.

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Experimental Part

1. N-[N$^{\alpha}$-(*Benzyloxycarbonyl*)-L-*valyl*]-N,N′-*diisopropylurea* (**1**) *and* N-[N$^{\alpha}$-(tert-*Butyloxycarbonyl*)-L-*valyl*]-N,N′-*dicyclohexylurea* (**2**) were prepared according to the precedures reported earlier [10] [11].

N-[N$^{\alpha}$-(*Benzyloxycarbonyl*)-L-*valyl*]-N′-(tert-*butyl*)-N-*ethylurea* (**3**). To a soln. of *N*$^{\alpha}$-(benzyloxycarbonyl)-L-valine (1.26 g, 5 mmol) in CH_2Cl_2 (15 ml), glycine ethyl ester hydrochloride (0.69 g, 5 mmol) and Et_3N (0.69 ml, 5 mmol) were added. To this mixture, *N*-(*tert*-butyl)-*N*′-ethylcarbodiimide (0.63 g, 5 mmol) in CH_2Cl_2 (10 ml) was added in three portions within 2 min, and the mixture was stirred overnight at r.t. The insoluble material was removed by filtration and the filtrate evaporated. The residue was dissolved in AcOEt (100 ml) and washed successively with 10% citric acid, sat. $NaHCO_3$ soln., and H_2O, and dried ($MgSO_4$). The solvent was evaporated. A sample (100 mg) of this material was subjected to chromatography on a 20 × 20-cm plate coated with silica gel *G* (*Merck*; 20 g). The products were separated as described earlier [11]. Three products were isolated: N$^{\alpha}$-(*benzyloxycarbony*)-L-*valyl-glycine ethyl ester* (44 mg, R_f 0.35, m.p. 168°), **3** (28 mg, R_f 0.85, m.p 76°; anal. calc. for $C_{20}H_{31}N_3O_4$ (377.5): C 63.64, H 8.28, N 11.13; found: C 64.04, H 8.42, N 11.27), and N-[N$^{\alpha}$-(*benzyloxycarbonyl*)-L-*valyl*]-N-tert-*butyl*-N′-*ethylurea* (14 mg, R_f 0.7, oil; anal. calc. for $C_{20}H_{31}N_3O_4$ (377.5): C 63.64, H 8.28, N 11.13; found: C 63.92, H 8.36, N 10.95).

2. *Peptides*. The synthesis and characterization of Nps-Lys(Boc)-[Lys(Boc)]$_4$Lys(Boc)-OChocb have already been described [17].

3. *X-Ray Diffraction.* N-*[N$^{\alpha}$-(Benzyloxycarbonyl)*-L-*valyl]*-N,N′-*diisopropylurea* (**1**; $C_{20}H_{31}N_3O_4$) crystallized from an acetone soln. in the orthorhombic system, space group $P2_12_12_1$ with $a = 25.278(2)$, $b = 11.056(1)$, and $c = 7.797(1)$ Å; $V = 2179.0$ Å^3; $Z = 4$; $D_c = 1.150$ g cm^{-3}; $\mu = 0.48$ cm^{-1}. The independent reflections (2998) were collected on a *Philips PW 1100* four-circle diffractometer, θ–2θ scan mode up to $2\theta = 50°$, Mo$K\alpha$ radiation monochromatized by a graphite crystal ($\lambda = 0.71069$ Å). The structure was solved by direct methods (MULTAN 80) [47] and refined by least-squares procedures. The refinement was carried out with anisotropic temperature factors for all non-H-atoms. Part of the H-atoms were found on a difference *Fourier* map, while the remaining ones were calculated but not refined. The final R factor for the 1442 considered observed reflections ($I \geq 3\sigma(I)$) was 0.062.

N-{N$^{\alpha}$-*[(*tert-*Butyloxy)carbonyl]*-L-*valyl*}-N,N′-*dicyclohexylurea* (**2**; $C_{33}H_{41}N_3O_4$) crystallized from acetone/H_2O in the monoclinic system, space group $P2_1$, with $a = 11.672(2)$, $b = 9.910(2)$, $c = 11.148(2)$ Å, $\beta = 95.0(2)°$; $V = 1284.6$ Å^3; $Z = 2$; $D_c = 1.095$ g cm^{-3}; $\mu = 0.43$ cm^{-1}. Independent reflections, 3280. The structure was solved by direct methods (SHELXS 86) [48]; temperature factors anisotropic for all non-H-atoms except for the five disordered C-atoms C(9), C(10), C(11), C(12), and C(13) of one cyclohexyl ring; H-atoms calculated and not refined; final R factor for the 1228 considered observed reflections ($I \geq 3\sigma(I)$), 0.124. All other data and methods were identical to those described for **1**. The relatively high values of the R factor and estimated standard deviations, to be ascribed to the small dimensions of the crystal (0.2 × 0.2 × 0.05 mm) and to the disorder of one cyclohexyl ring, were responsible for the poor quality of bond-length, bond-angle, and torsion-angle values; however, there are no doubts about the overall structure of **2**.

N-*[*N$^{\alpha}$-*(Benzyloxycarbonyl)*-L-*valyl]*-N′-*(*tert-*butyl)*-N-*ethylurea* (**3**; $C_{20}H_{31}N_3O_4$) crystallized from AcOEt/hexane in the monoclinic system, space group $P2_1$ with $a = 14.123(2)$, $b = 9.501(1)$, $c = 8.298(1)$ Å, $\beta = 103.0(2)$; $V = 1084.9$ Å^3; $Z = 2$; $D_c = 1.158$ g cm^{-3}; $\mu = 0.48$ cm^{-1}. Independent reflections, 2777; final R factor for the 1642 considered observed reflections ($I \geq 3\sigma(I)$) 0.086. All other data and methods were identical to those described above for **1**.

All calculations for the three structures were performed using the SHELX-76 program and related scattering factors [49]. The lists of final positional parameters, structure factors, and thermal parameters for **1**–**3** are available from the *Cambridge Crystallographic Data Center.*

4. *Spectroscopy.* IR spectra: *Perkin-Elmer* model *580 B* spectrophotometer, equipped with a *Perkin-Elmer* model *3600* data station and a model *660* printer; cell with path lenghts of 1.0 mm and CaF_2 windows; band positions accurate to ±1 cm^{-1}; CH_2Cl_2 from *Fluka.*

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