decolorized with charcoal and evaporated to dryness to yield brown crystals (10%). The product had infrared and ultraviolet spectra identical with that of an authentic sample of azoxybenzene.

Reduction of 1,4-Benzoquinone with IIb. IIb, 10 g (9.1% of copper(I) 14.2×10^{-3} mol of copper), was added to a solution containing 432 mg (4×10^{-3} mol) of 1,4-benzoquinone and 50 mL of 10% hydrochloric acid solution. The mixture was refluxed and stirred for 12 h. The IIa was removed by filtration and the filtrate was neutralized with dilute sodium hydroxide solution and extracted with ether. The ether layer was separated, dried (Na_2SO_4), treated with activated charcoal, and evaporated to dryness. The residue was 135 mg (31%) of white crystals, whose infrared spectrum was identical with that of an authentic hydroquinone sample. The copper content of the polymer after the reaction was 6.8%. Titration of reaction mixtures with cerium(IV) immediately subsequent to removal of IIa showed that yields were quantitative.

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References and Notes

(1) Taken in part from the reports submitted by Messrs. Kitoh and Walsworth in partial fulfillment of the requirements for the Master of Science degree, Clarkson College of Technology, 1977.
(2) Address correspondence to this author: Vice President for Academic Affairs, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801.
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Linear Oligopeptides. 59.[1] Stereochemical Analysis of *N-tert*-Butyloxycarbonyl-L-prolylsarcosine and *N-tert*-Butyloxycarbonylsarcosylsarcosine in the Solid State and in Solution

Ettore Benedetti,*[2a] Anna Ciajolo,[2a] Benedetto Di Blasio,[2a] Vincenzo Pavone,[2a] Carlo Pedone,[2a] Claudio Toniolo,[2b] and Gian Maria Bonora[2b]

Istituto Chimico, 80134 Napoli, Italy, and Centro per lo studio dei Biopolimeri, C.N.R., and Istituto di Chimica Organica, 35100 Padova, Italy. *Received November 22, 1978*

ABSTRACT: An analysis of the conformational properties of *N-tert*-butyloxycarbonyl-L-prolylsarcosine and *N-tert*-butyloxycarbonylsarcosylsarcosine was carried out in the solid state and in solution. The stereochemical preferences of the two N-protected dipeptides were found to be close under the experimental conditions examined. In the solid state a cis tertiary urethane bond and an intermolecular O–H···O=C (amide) hydrogen bond characterize the molecular and crystal structures. Even in a solvent of low polarity at high dilution the amounts of intramolecularly hydrogen-bonded forms, if any, appear to be negligible.

As a part of our continuing study[1,3-8] of the occurrence, both in the solid state and in solution, of the oxy analogues of the 3 → 1 and 4 → 1 intramolecularly hydrogen-bonded peptide conformations (also called oxy-C_7 and oxy-C_{10} forms, respectively), the present report provides information from infrared absorption (IR) and X-ray diffraction analysis of the conformational preferences of two *N-tert*-butyloxycarbonyl (*t*-Boc) dipeptides containing exclusively *N*-alkyl-α-amino acid residues, namely *t*-Boc-L-Pro-Sar-OH and *t*-Boc-Sar-Sar-OH.

On the basis of an IR absorption investigation in the solid state, Deber[9] has recently proposed for *t*-Boc-L-Pro-Sar-OH the possible formation of an antiparallel dimer, where the –OH proton of the –COOH group of each molecule is hydrogen bonded to the peptide C=O group of its neighbor, forming a 14-membered ring structure between two molecules, closed with two hydrogen bonds.

The only N-protected dipeptide of the aforementioned type (i.e., lacking amide protons) so far examined by X-ray diffraction is Z-L-Pro-Pro-OH[10] (Z stands for benzyloxycarbonyl–). The peptide backbone exhibits a sharp bend at the site of the cis bond between the N-blocking group and the first prolyl residue. Also, a network of intermolecular hydrogen bonds of the type O–H···O=C (urethane type) is formed in the crystal. In contrast, the free H_2^+-Sar-Sar-O^- peptide has the tertiary peptide bond in the cis configuration according to the X-ray diffraction study of this molecule carried out by Stezowski and Hughes.[11]

Experimental Section

Materials. The details of the synthesis of *t*-Boc-L-Pro-OH,[4] *t*-Boc-Sar-OH,[12] *t*-Boc-L-Pro-OMe (OMe stands for methoxy),[4] *t*-Boc-L-Pro-Sar-OMe,[5] *t*-Boc-L-Pro-Sar-OH,[5] *t*-Boc-Sar-OMe,[12] *t*-Boc-Sar-Sar-OMe,[12] and *t*-Boc-Sar-Sar-OH[12] have already been reported.

Ac-Sar-OH (where Ac is acetyl)[13] was prepared by reacting acetic anhydride with sarcosine at pH 8.5; the reaction mixture was brought to pH 3 with dilute HCl and evaporated to dryness under reduced pressure. The resulting product was dissolved in chloroform, dried over anhydrous sodium sulfate, filtered, and evaporated to small volume under reduced pressure, mp 134 °C.

Infrared Absorption. Infrared absorption spectra were recorded using a Perkin-Elmer Model 580 spectrophotometer. For the solution measurements a 10-cm cell was employed at low concentrations (~10^{-4} M), whereas cells with path lengths of 0.2, 0.1, and 0.05 mm were used for measurements at high concentrations (~10^{-2} M).

Trimethyl phosphate (TMP), deuteriochloroform (99.8% *d*), and deuterium oxide (99.9% *d*) were purchased from Merck, Darmstadt. For the solid measurements the KBr disk technique was employed. The band positions are accurate to ±1 cm^{-1}.

X-ray Diffraction. Crystals of *t*-Boc-L-Pro-Sar-OH and *t*-Boc-Sar-Sar-OH, both in the form of colorless needles, were grown from different organic solutions (acetone and ethyl acetate usually give better quality crystals).

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Table I
Crystal Data of t-Boc-L-Pro-Sar-OH and t-Boc-Sar-Sar-OH

	t-Boc-L-Pro-Sar-OH	t-Boc-Sar-Sar-OH
molecular formula	$C_{13}H_{22}N_2O_5$	$C_{11}H_{22}N_2O_5$
molecular weight	286.33	262.31
crystal system	orthorombic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$
Z, molecules/unit cell	4	4
a, Å	6.670 (3)	11.797 (2)
b, Å	13.987 (2)	9.768 (2)
c, Å	16.804 (4)	12.555 (3)
β, deg		106.19
V, Å^3	1567.7	1389.3
density, by flotation, g·cm^{-3}	1.21	1.25
density, calcd, g·cm^{-3}	1.213	1.254
radiation	Cu K_α, λ = 1.5418 Å	Cu K_α, λ = 1.5418 Å
no. of independent reflections	1204	1028
temp, °C	23, ambient	23, ambient

A CAD4 Enraf-Nonius diffractometer equipped with PDP-8 and PDP-11 digital computers was used for the data collection, structure determination, and refinement. The SDP package of crystallographic programs (structure determination programs) was thoroughly used. Unit cell parameters, orientation matrix, and intensity data collection for the two structures were carried out using a graphite monochromator and Cu K_α radiation. Crystallographic data are reported in Table I.

Data collection for t-Boc-L-Pro-Sar-OH and t-Boc-Sar-Sar-OH was carried out using the set of conditions reported in the following. An $\omega - 2\theta$ scan mode with a range of $(0.8 + 0.15 \tan \theta)°$ was chosen for the peak measurements; background counts were taken at each end of each scan. A distance crystal counter of 368 mm was used with a counter entrance aperture of 4 mm. The tube placed between the goniometer head and the detector was evacuated using a vacuum pump.

Prescan runs were made with a speed of 5 deg/min. Reflections with a net intensity $I \leq \sigma(I)0.5$ were flagged as "weak"; those having $I > \sigma(I)0.5$ were measured at lower speed (in the range 1–5 deg/min) depending on the value of $\sigma(I)/I$. The maximum time allowed for the scan was set to 60 s. Two intensity-control reflections were recorded every 60 min of X-ray exposure time; no significant change in their intensity was observed during data collection. Orientation checks were made with respect to the scattering vectors of four strong reflections every 200 reflections; reorientation was made using 25 high-angle reflections if displacement exceeded the calculated value by 0.15°.

A total of 1294 and 1438 reflections in the range 1–130 of 2θ, corresponding to one and two octants respectively for t-Boc-L-Pro-Sar-OH and t-Boc-Sar-Sar-OH, were collected; of these reflections 1204 and 1028 respectively had a net intensity greater than $2.0\sigma(I)$ and were considered as "observed". All reflections were corrected for Lorentz and polarization effects.

The structures were determined by means of the direct multisolution method given by Germain, Main, and Woolfson[14] in the program MULTAN, included in the SDP package. The 242 and 264 reflections with $E \geq 1.4$ and $E \geq 1.8$ were used respectively for t-Boc-L-Pro-Sar-OH and t-Boc-Sar-Sar-OH, with the 2000 largest Sayre's relationships in both cases. A starting set with three origin-fixing reflections and three arbitrary phase reflections, one of which fixed also the enantiomorph, produced 32 different solutions for t-Boc-L-Pro-Sar-OH. The set of phases presenting the highest combined figure of merit led to an E map from which the positions of all the non-hydrogen atoms were recovered. For t-Boc-Sar-Sar-OH a starting set with three origin-fixing reflections and four arbitrary phase reflections produced 16 different solutions, three of which presented the highest combined figure of merit.

The corresponding E map again led to the determination of the positional parameters of all non-hydrogen atoms.

Refinement by a least-squares procedure with weights $w = 1/\sigma(F_o^2)$, anisotropic temperature factors for C, N, and O atoms, and isotropic temperature factors for hydrogen atoms in their calculated stereochemically expected positions led to final R values of 0.058 and 0.063 in t-Boc-L-Pro-Sar-OH and t-Boc-Sar-Sar-OH, respectively, for all reflections with $F_o^2 > 2\sigma(F_o^2)$. In both cases the parameters of the hydrogen atoms were kept fixed with the isotropic temperature factor for each hydrogen equal to that of the carrier atom. Refinement was ended when the maximum shift in the atomic coordinates and anisotropic thermal parameters were less than $^1/_5$ and $^1/_3$ of the corresponding standard deviations, respectively. Atomic scattering factors for all atomic species were calculated from Cramer and Waber.[15] All calculations were carried out on a PDP-11 digital computer using the SDP system.

The final atomic parameters for both structures are reported in Table II.

Results and Discussion

Solid-State Conformational Analysis. The IR absorption data of t-Boc-L-Pro-Sar-OH and t-Boc-Sar-Sar-OH, their derivatives, and model compounds in the solid state are listed in Table III. The spectral pattern of the t-Boc-L-Pro-Sar-OH matches closely that reported by Deber.[9] It is evident that in general the spectra change only slightly on changing the solvent from which the solid compound was obtained.

As far as the two N-protected dipeptides are concerned, the following conclusions can be drawn:

(i) The acid C=O stretching region reveals bands higher than 1740 cm^{-1}, i.e., in the region where free carbonyl absorptions are usually seen.[1,9] This suggestion is substantiated by the position of the corresponding bands of t-Boc-L-Pro-OH (at 1753 and 1740 cm^{-1}) which is known to have a free acid C=O group in the solid state.[16]

(ii) The tertiary urethane C=O stretching vibrations are located at a frequency ≥1684 cm^{-1}. The position of the corresponding bands in the N- and C-protected derivatives and model compounds (at 1710–1698 cm^{-1}) supports our contention that all these absorptions pertain to free carbonyls.[9] Indirect evidence is given by the frequencies of the bands of the bonded tertiary urethane C=O group of t-Boc-L-Pro-OH[17] and t-Boc-Sar-OH which are located at 1638 and 1646 cm^{-1}, respectively.

(iii) The tertiary amide C=O stretching bands are visible at low frequencies, particularly that of t-Boc-L-Pro-Sar-OH (in the 1612–1604-cm^{-1} region). According to Deber's assignment[9] this absorption must be due to the hydrogen-bonded peptide carbonyl. The single band below 1700 cm^{-1} of Ac-Sar-OH is seen at 1603 cm^{-1}, and the only N-acetyl-N-alkyl-α-amino acid so far investigated by X-ray diffraction shows a strong intermolecular hydrogen bond connecting the O–H of one molecule to the oxygen of the N-acetyl group of a neighboring molecule.[18] The corresponding bands of N- and C-blocked dipeptides fall at 1678–1662 cm^{-1}.

From the IR absorption results we conclude that a hydrogen bond exists in the solid state between the O–H hydrogen and the amide oxygen in both t-Boc-L-Pro-Sar-OH and t-Boc-Sar-Sar-OH. However, this stereochemical analysis cannot solve the ambiguity between the various possible types of hydrogen bonds, whether (i) intramolecular, forming a folded oxy-C_7 structure,[1,4,7,8] or (ii) intermolecular, forming an antiparallel dimer, as suggested by Deber,[9] or (iii) intermolecular, forming polymeric structures.

In order to define unambiguously the structure of t-Boc-L-Pro-Sar-OH and t-Boc-Sar-Sar-OH in the solid state we have examined the two N-protected dipeptides by X-ray diffraction.

In Figures 1 and 2 the molecular structures of t-Boc-L-Pro-Sar-OH and t-Boc-Sar-Sar-OH are given together with the final geometrical parameters. Bond lengths and bond angles involving similar groups in the two molecules

Table II
Final Atomic Parameters for *t*-Boc-L-Pro-Sar-OH and *t*-Boc-Sar-Sar-OH[a]

t-Boc-L-Pro-Sar-OH

atom	*X*	*Y*	*Z*	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
O(5)	0.3823 (5)	0.1446 (2)	0.1480 (2)	0.0332 (8)	0.0074 (2)	0.0041 (1)	−0.0102 (7)	0.0002 (5)	−0.0018 (2)
O(4)	0.6810 (6)	0.2008 (2)	0.1037 (2)	0.0423 (9)	0.0100 (2)	0.0063 (2)	−0.0242 (7)	0.0063 (7)	−0.0042 (3)
O(1)	0.4504 (4)	−0.0585 (2)	0.0509 (2)	0.0210 (6)	0.0053 (1)	0.0070 (1)	0.0012 (6)	−0.0014 (6)	0.0007 (2)
O(2)	0.0708 (5)	−0.3163 (2)	0.0569 (2)	0.0332 (8)	0.0065 (2)	0.0062 (1)	−0.0086 (7)	−0.0041 (6)	0.0027 (2)
O(3)	0.0737 (5)	−0.2025 (2)	0.0358 (2)	0.0443 (11)	0.0071 (2)	0.0046 (1)	−0.0064 (8)	−0.0026 (7)	0.0013 (2)
N_1	0.4534 (7)	0.1335 (2)	0.0211 (2)	0.0475 (12)	0.0049 (2)	0.0039 (1)	−0.0072 (9)	0.0015 (8)	−0.0006 (2)
N_2	0.1238 (5)	−0.0613 (3)	0.0758 (2)	0.0224 (8)	0.0071 (2)	0.0058 (2)	−0.0029 (8)	−0.0017 (7)	−0.0020 (3)
C(1)	0.2142 (9)	0.1343 (5)	0.2683 (3)	0.0423 (16)	0.0125 (4)	0.0061 (2)	0.0013 (17)	0.0067 (12)	0.0002 (6)
C(2)	0.5829 (8)	0.1106 (5)	0.2663 (3)	0.0390 (16)	0.0135 (5)	0.0061 (2)	0.0098 (16)	−0.0001 (12)	0.0029 (5)
C(3)	0.4409 (10)	0.2732 (4)	0.2439 (3)	0.0641 (24)	0.0090 (3)	0.0048 (2)	−0.0110 (17)	0.0006 (13)	−0.0037 (4)
C(4)	0.4102 (7)	0.1671 (3)	0.2331 (2)	0.0346 (13)	0.0080 (3)	0.0041 (2)	−0.0061 (12)	0.0011 (9)	−0.0006 (4)
C(5)	0.5217 (7)	0.1629 (3)	0.0919 (2)	0.0367 (12)	0.0051 (2)	0.0041 (1)	−0.0084 (9)	0.0012 (8)	−0.0006 (3)
C_1^{δ}	0.5651 (11)	0.1473 (3)	−0.0520 (3)	0.0750 (25)	0.0061 (3)	0.0046 (2)	−0.0078 (16)	0.0052 (13)	0.0002 (4)
C_1^{α}	0.2667 (7)	0.0797 (3)	0.0110 (2)	0.0374 (12)	0.0044 (2)	0.0052 (2)	0.0023 (10)	−0.0089 (8)	−0.0018 (3)
C_1'	0.2871 (6)	−0.0184 (3)	0.0485 (2)	0.0212 (8)	0.0047 (2)	0.0039 (1)	−0.0001 (8)	−0.0030 (6)	−0.0012 (3)
C(6)	0.0794 (8)	−0.0211 (6)	0.0714 (5)	0.0228 (13)	0.0131 (5)	0.0147 (5)	0.0023 (14)	0.0036 (15)	−0.0068 (8)
C_2^{α}	0.1400 (8)	−0.1613 (3)	0.0986 (3)	0.0342 (12)	0.0077 (3)	0.0050 (2)	−0.0117 (10)	−0.0025 (9)	0.0007 (4)
C_2'	0.0908 (6)	−0.2272 (3)	0.0310 (2)	0.0218 (9)	0.0065 (2)	0.0046 (1)	−0.0037 (8)	0.0007 (7)	0.0013 (3)
C_1^{β}	0.2498 (11)	0.0684 (3)	−0.0796 (3)	0.0793 (24)	0.0068 (3)	0.0057 (2)	−0.0046 (17)	−0.0189 (12)	0.0013 (4)
C_1^{γ}	0.4540 (12)	0.0803 (4)	0.1091 (3)	0.0787 (27)	0.0100 (3)	0.0042 (2)	−0.0048 (20)	−0.0006 (14)	−0.0030 (4)

atom	*X*	*Y*	*Z*	*B*	atom	*X*	*Y*	*Z*	*B*
H(1)-C(1)	0.1982	0.0598	0.2592	6.83	H(2)-C_1^{δ}	0.5585	0.2189	−0.0712	6.43
H(2)-C(1)	0.0941	0.1695	0.2402	6.83	H(1)-C_1^{γ}	0.5275	0.0145	−0.1117	8.80
H(3)-C(1)	0.2114	0.1486	0.3293	6.83	H(2)-C_1^{γ}	0.4512	0.1114	−0.1664	8.80
H(1)-C(2)	0.5559	0.0375	0.2579	6.75	H(1)-C_1^{β}	0.1544	0.1206	−0.1038	7.14
H(2)-C(2)	0.5962	0.1252	0.3275	6.75	H(2)-C_1^{β}	0.1957	0.0001	−0.0943	7.14
H(3)-C(2)	0.7155	0.1304	0.2372	6.75	H(1)-C(6)	−0.1831	−0.0678	0.0972	8.23
H(1)-C(3)	0.3188	0.3105	0.2194	6.77	H(2)-C(6)	−0.1195	−0.0087	0.0115	8.23
H(2)-C(3)	0.5732	0.2943	0.2141	6.77	H(3)-C(6)	−0.0850	0.0454	0.1020	8.23
H(3)-C(3)	0.4539	0.2891	0.3044	6.77	H(1)-C_2^{α}	0.0401	−0.1743	0.1461	5.23
H-C_1^{α}	0.1439	0.1175	0.0345	4.98	H(2)-C_2^{α}	0.2874	−0.1747	0.1182	5.23
H(1)-C_1^{δ}	0.7157	0.1271	−0.0452	6.43	H-O(2)	0.0361	−0.3613	0.0087	5.38

t-Boc-Sar-Sar-OH

atom	*X*	*Y*	*Z*	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
O(5)	0.3277 (4)	0.0091 (4)	0.0445 (3)	0.0078 (4)	0.0075 (5)	0.0063 (3)	0.0013 (8)	0.0036 (5)	0.0003 (7)
O(2)	−0.0875 (4)	−0.0488 (5)	−0.3832 (3)	0.0076 (4)	0.0130 (6)	0.0082 (3)	−0.0075 (9)	−0.0021 (6)	0.0036 (8)
O(1)	0.1951 (4)	0.2174 (5)	−0.1285 (3)	0.0075 (4)	0.0115 (6)	0.0067 (3)	0.0072 (8)	0.0024 (6)	−0.0028 (7)
O(3)	0.0709 (4)	−0.1370 (5)	0.2621 (4)	0.0083 (4)	0.0101 (6)	0.0111 (4)	−0.0043 (9)	0.0013 (7)	0.0051 (8)
O(4)	0.4024 (4)	0.1826 (5)	0.1635 (3)	0.0119 (5)	0.0155 (7)	0.0057 (3)	−0.0026 (11)	0.0015 (6)	−0.0068 (8)
N_1	0.4229 (4)	0.1778 (5)	−0.0116 (4)	0.0057 (4)	0.0083 (7)	0.0066 (4)	−0.0043 (9)	0.0015 (6)	−0.0024 (8)
N_2	0.2056 (4)	0.0873 (5)	−0.2739 (4)	0.0063 (4)	0.0075 (6)	0.0063 (4)	−0.0043 (9)	0.0016 (6)	−0.0025 (8)
C_1^{α}	0.3842 (5)	0.1184 (5)	−0.1209 (5)	0.0047 (5)	0.0130 (9)	0.0050 (4)	0.006 (1)	−0.0009 (7)	−0.002 (1)
C_1'	0.2496 (5)	0.3529 (6)	0.3249 (5)	0.0062 (5)	0.0069 (7)	0.0066 (4)	−0.001 (1)	0.0052 (7)	0.003 (1)
C(5)	0.3841 (5)	0.1279 (7)	0.0733 (5)	0.0053 (5)	0.0097 (9)	0.0074 (5)	0.004 (1)	−0.006 (8)	0.002 (1)
C_2'	0.0230 (6)	−0.0444 (7)	−0.3190 (5)	0.0074 (6)	0.0100 (9)	0.0058 (4)	−0.002 (1)	0.0027 (8)	−0.002 (1)

atom	X	Y	Z	B	atom	X	Y	Z	B
C(7)	0.4776 (7)	0.3095 (9)	0.0006 (6)	0.0109 (8)	0.0167 (12)	0.0099 (6)	−0.008 (2)	0.0058 (11)	−0.003 (2)
C_2^{α}	0.0795 (6)	0.0946 (7)	−0.3257 (5)	0.0082 (6)	0.0101 (9)	−0.0066 (5)	−0.003 (1)	0.0002 (9)	0.001 (1)
C(4)	0.2462 (6)	−0.0467 (7)	0.1039 (5)	0.0076 (6)	0.0104 (9)	0.0056 (4)	0.001 (1)	0.0030 (8)	0.003 (1)
C(3)	0.3152 (7)	−0.0953 (9)	0.2188 (6)	0.0117 (8)	0.0194 (13)	0.0071 (6)	−0.000 (2)	0.0017 (10)	0.006 (1)
C(6)	0.2757 (6)	0.0078 (8)	−0.3312 (5)	0.0108 (7)	0.0121 (10)	0.0092 (5)	−0.007 (1)	0.0079 (9)	−0.009 (1)
C(1)	0.1896 (7)	−0.1642 (8)	0.0311 (5)	0.0113 (7)	0.0117 (10)	0.0087 (5)	−0.003 (2)	0.0068 (10)	0.002 (1)
C(2)	0.1550 (6)	0.0596 (8)	0.1083 (6)	0.0093 (7)	0.0136 (11)	0.0100 (6)	0.003 (2)	0.0052 (10)	−0.000 (1)
H–O(2)	−0.1233	−0.1453	−0.3760	4.70	H(3)–C(7)	0.4170	0.3843	0.0106	5.88
H(1)–C_2^{α}	0.0634	0.1218	−0.4093	3.83	H(1)–C(1)	0.1295	−0.2143	0.0656	5.09
H(2)–C_2^{α}	0.0413	0.1674	−0.2852	3.83	H(2)–C(1)	0.2560	−0.2350	0.0255	5.09
H(1)–C(6)	0.2475	0.0294	−0.4163	5.60	H(3)–C(1)	0.1465	−0.1285	−0.0482	5.09
H(2)–C(6)	0.2652	−0.0967	−0.3180	5.60	H(1)–C(2)	0.0966	0.0196	0.1504	5.39
H(3)–C(6)	0.3652	0.0347	−0.2997	5.60	H(2)–C(2)	0.1070	0.0863	0.0271	5.39
H(1)–C_1^{α}	0.4273	0.0414	−0.1511	3.29	H(3)–C(2)	0.1970	0.1465	0.1500	5.39
H(2)–C_1^{α}	0.3277	0.1719	−0.1902	3.29	H(1)–C(3)	0.2567	−0.1355	0.2602	5.60
H(1)–C(7)	0.5024	0.3324	−0.0723	5.88	H(2)–C(3)	0.3615	−0.0126	0.2635	5.60
H(2)–C(7)	0.5521	0.3108	0.0686	5.88	H(3)–C(3)	0.3751	−0.1719	0.2110	5.60

[a] The form of the anisotropic thermal parameter is: $\exp - [\beta(1,1)\cdot h\cdot h + \beta(2,2)\cdot k\cdot k + \beta(3,3)\cdot l\cdot l + \beta(1,2)\cdot h\cdot k + \beta(1,3)\cdot h\cdot l + \beta(2,3)\cdot k\cdot l]$.

show close analogies and are in excellent agreement with literature data.[6,19] As an example, the *tert*-butyl groups and the urethane moiety in both compounds exhibit in their geometry the same features encountered in all the other *N*-*t*-Boc derivatives of α-amino acids,[19] such as the staggering of the methyl groups with respect to O(5) and the pinching of the O(5)–C(4)–C(1) angle (102.5°) coupled with the opening of the C(4)–O(5)–C(5) angle (122–123°). These deformations afford the relief in the intramolecular contacts among the carbonyl group of the urethane moiety and the methyl groups of the crowded *tert*-butyl terminal.

The C–O distances in the three types of carbonyls (Figures 1a and 2a) correlate well with the IR absorption data listed in Table III, the highest frequencies in the spectrum (1768–1741 cm^{-1}) being identified with the carboxylate groupings C_2'–O(3), which show the shortest C–O distances (1.18–1.19 Å), and the lowest frequencies (1612–1604 cm^{-1} for *t*-Boc-L-Pro-Sar-OH and 1639–1637 cm^{-1} for *t*-Boc-Sar-Sar-OH) with the amide C_1'–O(1) groupings, which show the longest distances (1.225 and 1.221 Å, respectively).

The close analogy between the two structures is also reflected in their overall conformation and crystal structure. Table IV summarizes all internal rotation angles for *t*-Boc-L-Pro-Sar-OH and *t*-Boc-Sar-Sar-OH while in Table V a comparison of some of these conformational parameters[20] with the corresponding angles of the structures of *t*-Boc-L-Pro-Gly-OH,[5] *t*-Boc-Sar-Gly-OBzl (OBzl stands for benzoyloxy),[21] and Z-L-Pro-L-Pro-OH,[10] recently reported, is given. The conformation of the peptide chain is defined by the angles ω_1, φ_1, ψ_1, ω_2, φ_2, and ψ_2* (for these compounds the ψ_2* notation corresponds to the N–C^{α}–C′–O(2) rotation angle). In all structures the tertiary amide group of the urethane moiety presents the cis configuration ($3° \leq \omega_1 \leq 12°$); this feature seems to be common to most of the *N*-*t*-Boc derivatives of the *N*-alkylated α-amino acids.[6,19]

The main difference in the conformation of *t*-Boc-L-Pro-Sar-OH and *t*-Boc-Sar-Sar-OH is observed in the φ_2 angle which is −91 and 107° for the two structures, respectively. These two conformations correspond to the two almost symmetrical orientations of the C-terminal carboxylic group with respect to the plane of the preceding amide moiety. Thus, the intramolecular contacts in this portion of the two molecules remain almost the same (for example, the O(3)···C(6) distances being 3.3 and 3.1 Å in *t*-Boc-L-Pro-Sar-OH and *t*-Boc-Sar-Sar-OH, respectively). It is also worth noting that the overall conformation observed for *t*-Boc-L-Pro-Sar-OH is in good agreement with those of *t*-Boc-L-Pro-Gly-OH,[5] *t*-Boc-Sar-Gly-OBzl,[21] and Z-L-Pro-L-Pro-OH,[10] even if in these four structures a different system of hydrogen bonds held the molecules together in the crystal state.

The values of φ_2 and ψ_2* angles in *t*-Boc-Sar-Sar-OH (107 and 168°, respectively) lie outside the "allowed" regions in the Ramachandran plot. These unusual figures on the other hand are not surprising, occurring also for (some) glycyl residues in *t*-Boc-Gly-L-Pro-OH,[3,22] *t*-Boc-L-Cys-(Bzl)-Gly-OMe,[23] H_2^+-Gly-L-Phe-Gly-O^-·H_2O,[24] and Z-(*p*-Br)-Gly-L-Pro-L-Leu-Gly-OH.[25] In addition, the φ_2 and ψ_2* values found for *t*-Boc-Sar-Sar-OH correspond in the conformational energy map of a sarcosine dipeptide with a cis-trans configuration for the two amide bonds to one of the calculated minima.[26] Different steric hindrance coupled with the need of achieving the energetically most favorable formation of hydrogen bonds should be responsible in each case for the observed conformation.

Table III
Infrared Absorption Data (cm^{-1}) for *t*-Boc-L-Pro-Sar-OH, *t*-Boc-Sar-Sar-OH, Their Derivatives, and Model Compounds in the Solid State

compd	acid or ester C=O stretching	urethane C=O stretching	amide C=O stretching
t-Boc-L-Pro-Sar-OH	(i)[a] 1764, 1746	1699, 1689	1606
	(ii)[b] 1768, 1751	1704, 1693	1612
	(iii)[c] 1750 (split)	1688	1604
t-Boc-L-Pro-Sar-OMe	(i)[a] 1750	1698	1662
	(ii)[d] 1754	1700	1669
t-Boc-Sar-Sar-OH	(i)[a] 1756 (s),[e] 1741	1700 (s),[e] 1684	1639
	(ii)[f] 1759, 1741	1700 (s),[e] 1687	1637
t-Boc-Sar-Sar-OMe	(i)[a] 1752	1698	1670
	(ii)[g] 1758	1709	1678
t-Boc-L-Pro-OH	1759 (s),[e] 1740[h]	1699 (vw),[i] 1638	
t-Boc-L-Pro-OMe	1752[l]	1708	
t-Boc-Sar-OH	1764,[h] 1746	1705 (vw),[i] 1646	
t-Boc-Sar-OMe	(i)[g] 1759	1707	
	(ii)[m] 1765	1700	
Ac-Sar-OH	1766,[l] 1736		1603

[a] From acetone; this work. [b] From ethyl acetate–petroleum ether; ref 5. [c] Reference 9. [d] From diethyl ether–petroleum ether; ref 5. [e] s = shoulder. [f] This work. [g] Neat; ref 12. [h] Reference 1. [i] vw = very weak. [l] Neat; ref 1. [m] Reference 16.

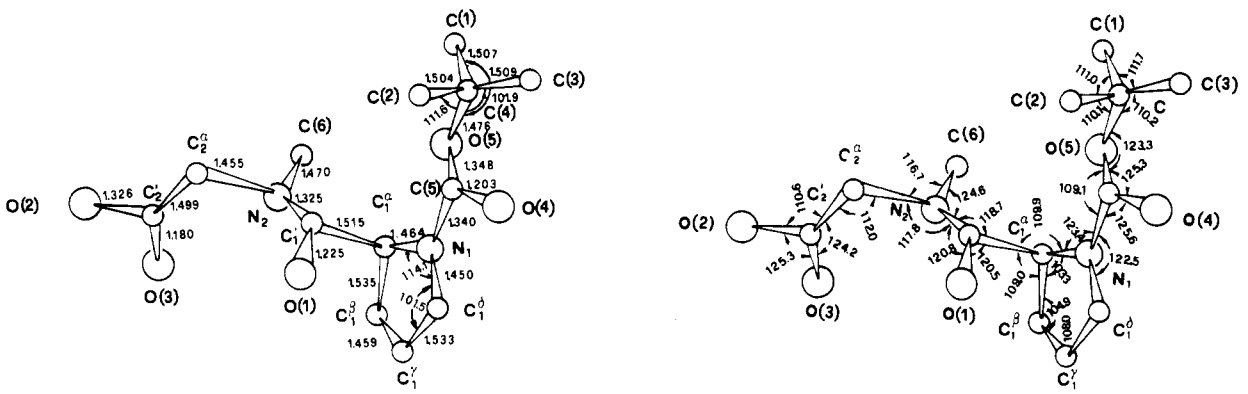

Figure 1. Molecular structure of *t*-Boc-L-Pro-Sar-OH showing bond lengths and bond angles. The average esd's of bond length and bond angles are 0.004 Å and 0.8°, respectively.

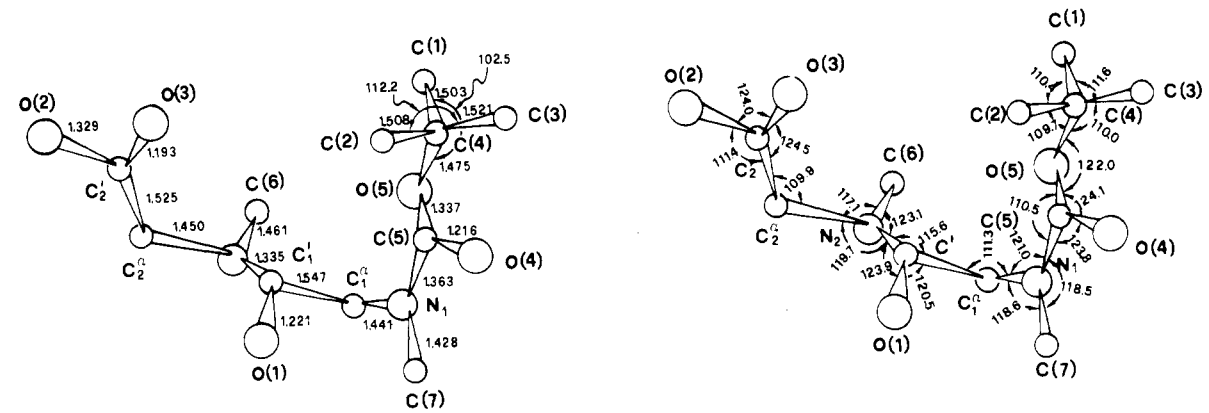

Figure 2. Molecular structure of *t*-Boc-Sar-Sar-OH, showing bond lengths and bond angles; their esd's are on the average the same as that reported in Figure 1.

The pyrrolidine ring of the prolyl residue in *t*-Boc-L-Pro-Sar-OH presents γ puckering, C^{γ}-endo conformation,[27,28] with the C^{γ} atom 0.42 Å out of the best plane passing through the other four atoms of the ring. The restricted φ angle of the prolyl residue is −67°. The carboxylic group of *t*-Boc-L-Pro-Sar-OH and *t*-Boc-Sar-Sar-OH adopt the preferred syn-planar conformation with respect to the C^{α}–N bond[29] (the internal rotation angles O(3)–C_2'–C_2^{α}–N_2 have values of 12 and −13°, respectively).

In both molecules the C(4)–O(5) bond of the urethane moiety is in the usual trans arrangement relative to the C(5)–N_1 bond; this feature, accompanied by the cis configuration of the tertiary urethane group, allows us to classify the urethane groups of these two molecules as type a in Figure 2 of ref 1.

The system of hydrogen bonds in the crystal structures of *t*-Boc-L-Pro-Sar-OH and *t*-Boc-Sar-Sar-OH is similar, but obviously not the same, since the molecules do not exhibit identical conformations in the crystal state. In both compounds the molecules form long rows through the formation of one intermolecular hydrogen bond of the type O–H···O (in both cases the O···O distance is 2.64 Å, i.e., within the most probable range for O–H···O hydrogen bonds in the crystal state with a carbonyl group as hy-

Table IV
Internal Rotation Angles (deg) for t-Boc-L-Pro-Sar-OH and t-Boc-Sar-Sar-OH

angle	t-Boc-L-Pro-Sar-OH	t-Boc-Sar-Sar-OH	angle	t-Boc-L-Pro-Sar-OH	t-Boc-Sar-Sar-OH
$O(2)-C_2'-C_2^\alpha-N_2$	−169	168	$N_1-C(5)-O(5)-C(4)$	179	161
$O(3)-C_2'-C_2^\alpha-N_2$	12	−13	$O(4)-C(5)-O(5)-C(4)$	−2	−21
$C_2'-C_2^\alpha-N_2-C(6)$	78	−70	$C(5)-O(5)-C(4)-C(1)$	179	190
$C_2'-C_2^\alpha-N_2-C_1'$	−91	107	$C(5)-O(5)-C(4)-C(2)$	−63	−53
$C_2^\alpha-N_2-C_1'-O(1)$	−8	5	$C(5)-O(5)-C(4)-C(3)$	61	71
$C_2^\alpha-N_2-C_1'-C_1^\alpha$	170	187	$O(1)-C_1'-C_1^\alpha-C_1^\beta$	82	
$N_2-C_1'-C_1^\alpha-N_1$	152	175	$C_1'-C_1^\alpha-C_1^\beta-C_1^\gamma$	−95	
$C(6)-N_2-C_1'-O(1)$	183	182	$C(5)-N_1-C_1^\delta-C_1^\gamma$	166	
$C(6)-N_2-C_1'-C_1^\alpha$	1	5	$C(5)-N_1-C_1^\alpha-C_1^\beta$	177	
$O(1)-C_1'-C_1^\alpha-N_1$	−31	−3	$N_2-C_1'-C_1^\alpha-C_1^\beta$	−95	
$C_1'-C_1^\alpha-N_1-C(7)^a$	110	96	$C_1^\beta-C_1^\alpha-N_1-C_1^\delta$	−7	
$C_1'-C_1^\alpha-N_1-C(5)$	−67	−69	$N_1-C_1^\alpha-C_1^\beta-C_1^\gamma$	22	
$C_1^\alpha-N_1-C(5)-O(4)$	174	171	$C_1^\alpha-C_1^\beta-C_1^\gamma-C_1^\delta$	−30	
$C_1^\alpha-N_1-C(5)-O(5)$	−7	−11	$C_1^\beta-C_1^\gamma-C_1^\delta-N_1$	25	
$C(7)-N_1-C(5)-O(4)^a$	−2	7	$C_1^\gamma-C_1^\delta-N_1-C_1^\alpha$	−11	
$C(7)-N_1-C(5)-O(5)^a$	177	185			

[a] In t-Boc-L-Pro-Sar-OH for this angle C(7) corresponds to C_1^δ.

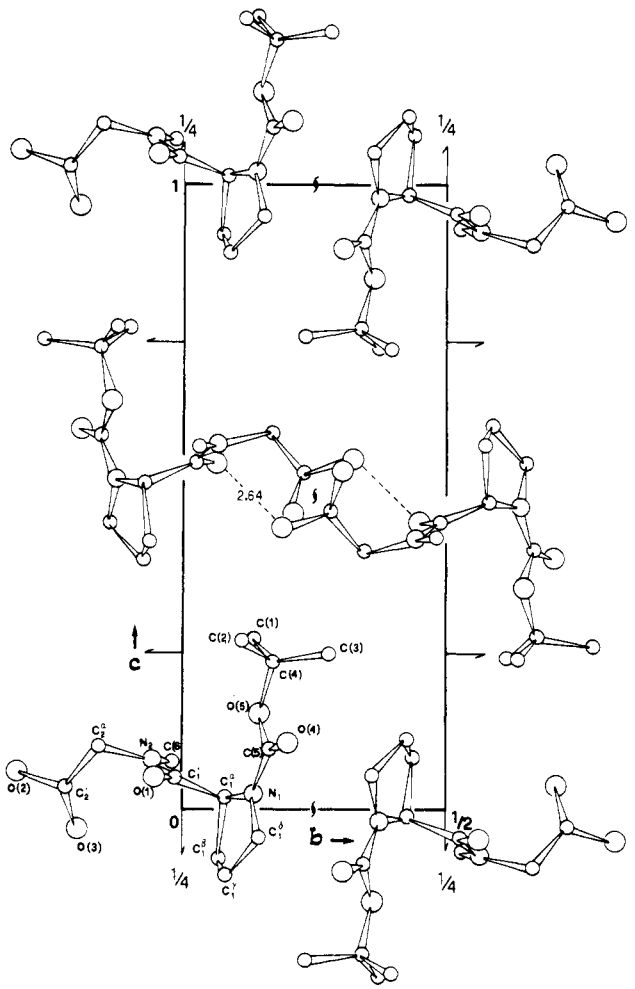

Figure 3. Mode of packing of t-Boc-L-Pro-Sar-OH as projected down the a axis. The hydrogen bonds are indicated as dashed lines.

drogen acceptor)[30] between the hydroxyl group of the –COOH moiety of one molecule with the oxygen atom of the amide carbonyl of another molecule related by a screw axis (along the a axis in t-Boc-L-Pro-Sar-OH and along the b axis in t-Boc-Sar-Sar-OH). The modes of packing for the two structures are illustrated in Figures 3 and 4, respectively. In this context, it should be recalled that a different situation is shown by Z-L-Pro-L-Pro-OH,[10] the only N-protected dipeptide formed by two N-alkyl-α-amino acid residues, outside those described in this paper, so far examined by X-ray diffraction (the hydrogen acceptor of the O–H···O intermolecular hydrogen bond being the carbonyl group of the urethane moiety).

Table V
Comparison of Conformational Angles (deg) Defining the Peptide Chain for t-Boc-L-Pro-Sar-OH, t-Boc-Sar-Sar-OH, t-Boc-L-Pro-Gly-OH,[5] t-Boc-Sar-Gly-OBzl,[20] and Z-L-Pro-L-Pro-OH[10]

angle	Pro-Sar	Sar-Sar	Pro-Gly	Sar-Gly	Pro-Pro
ω_1	−7	−11	−12	−12	3
φ_1	−67	−69	−61	−72	−65
ψ_1	152	175	147	154	155
ω_2	170	187	167	167	−179.6
φ_2	−91	107	−67	−81	−53
$\psi_2{}^a$	191	168	162	186	141

[a] See text for the explanation.

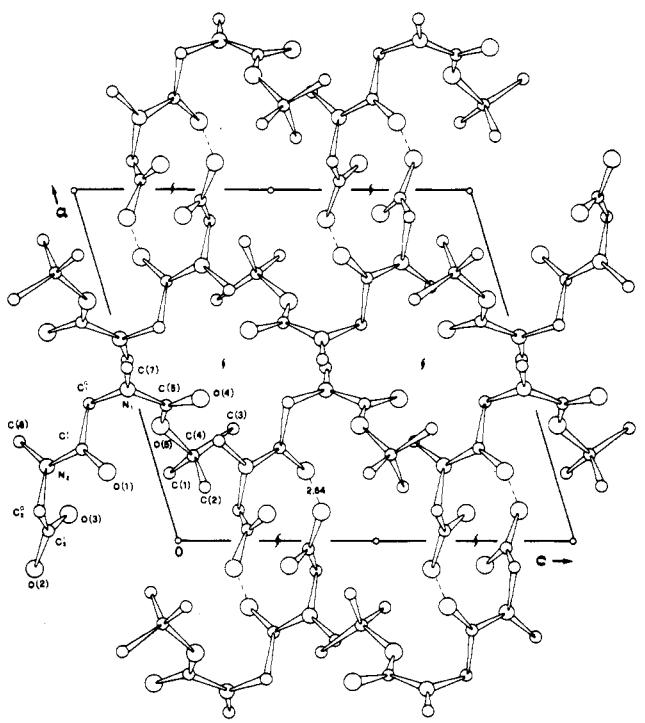

Figure 4. Mode of packing of the molecules of t-Boc-Sar-Sar-OH projected down the b axis. The hydrogen bonds are indicated as dashed lines.

To summarize, in both t-Boc-L-Pro-Sar-OH and t-Boc-Sar-Sar-OH in the solid state the oxy-C_7 structure

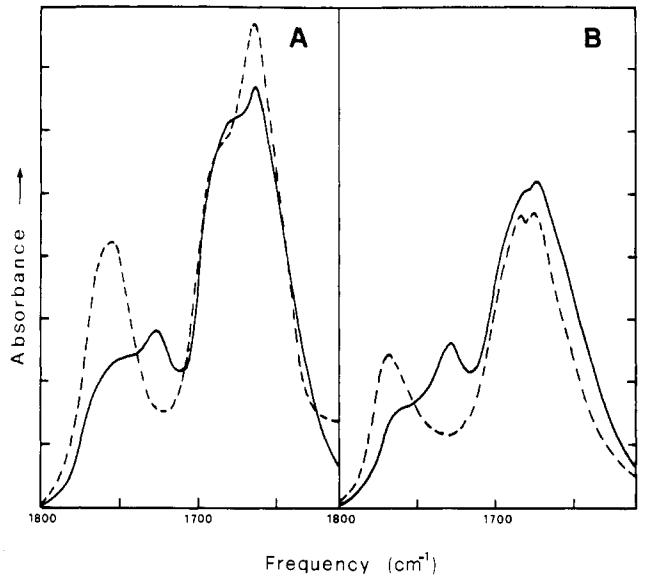

Figure 5. Infrared absorption spectra of *t*-Boc-L-Pro-Sar-OH (A) and *t*-Boc-Sar-Sar-OH (B) in deuteriochloroform at 20 °C, concentration 3×10^{-2} M (—) and 4.6×10^{-4} M (---).

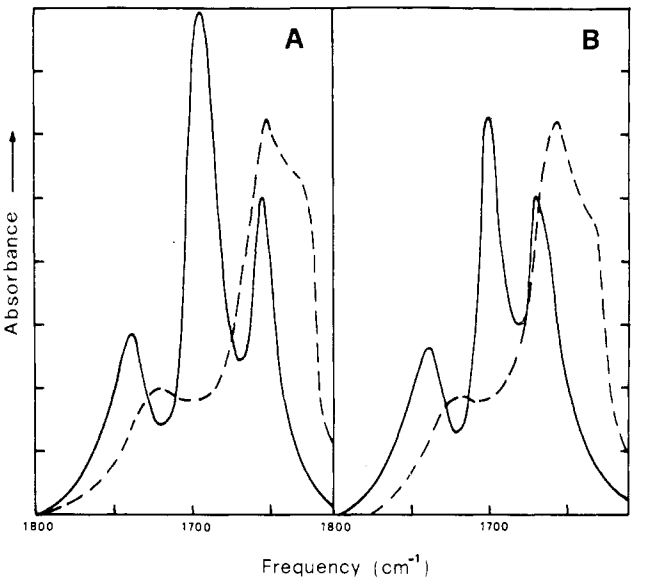

Figure 6. Infrared absorption spectra of *t*-Boc-L-Pro-Sar-OH (A) and *t*-Boc-Sar-Sar-OH (B) in TMP (—) and D_2O (---), concentration 3×10^{-2} M.

containing an intramolecular O–H···O hydrogen bond,[1,4,7,8] and the antiparallel dimer formed by two intermolecular hydrogen bonds, proposed by Deber[9] for the former compound, appear to be absent. The third possibility, postulated on the basis of the IR absorption data, was shown to be the correct one.

Solution Conformational Analysis. In order to investigate the conformational properties of *t*-Boc-L-Pro-Sar-OH and *t*-Boc-Sar-Sar-OH in solution we carried out an IR absorption analysis in solvents of divergent polarity and hydrogen-bonding properties and at different concentrations. The spectra obtained are shown in Figures 5 and 6. The interpretation of the results is complicated by the cis-trans isomerism around the tertiary urethane[31] and amide bonds. In addition, various types of intramolecularly hydrogen-bonded forms (oxy-C_7 and oxy-C_{10} forms)[1,3-5,7,8] and intermolecularly hydrogen-bonded aggregated or solvated species can account for the spectral properties of the two molecules.

In deuteriochloroform at a 3×10^{-2} M concentration (Figure 5) bands at 1761–1751, 1729–1728, 1682, and 1674–1665 cm^{-1} are visible. They were assigned respectively to free carbonyls of the COOH groups,[1,32] hydrogen-bonded carbonyls of the –COOH groups,[1,32] free carbonyls of the tertiary urethane groups, and free carbonyls of the tertiary amide groups.[33] This conclusion is corroborated by (i) the vibrations shown in the same solvent (not reported in the figure) by the corresponding –OMe C-protected derivatives (lacking acid hydrogens) (at 1750–1748 cm^{-1}, ester carbonyl; 1683 cm^{-1}, urethane carbonyl; and 1672–1666 cm^{-1}, amide carbonyl), and (ii) the spectra of the dilute solutions (at 4.6×10^{-4} M concentration) (Figure 5), characterized by the disappearance of the 1729–1728-cm^{-1} absorption and the constancy of the position of urethane and amide C=O vibrations. Hence, it may be reasonably suggested that in deuteriochloroform at high concentration the type of association which occurs is similar in both compounds but different from that found in the solid state; in addition at low concentration, i.e., in the absence of associated species, in both cases there is no evidence of the onset of intramolecularly hydrogen-bonded species to a considerable extent.[9]

In solvents of higher polarity and the capability of forming hydrogen bonds with the solute as hydrogen acceptor (TMP) or donor (water) (Figure 6), the conformational preferences of the molecules change dramatically.

In TMP only a minor amount of species with free acid carbonyl (shoulder near 1760 cm^{-1}) is visible, most of the molecules being fully solvated (1738, 1700–1697, and 1670–1664-cm^{-1} bands, due to free C=O groups of –COOH moieties with a O–H···O=P hydrogen bond, free tertiary urethane C=O groups, and free tertiary amide C=O groups, respectively).[1] The locations of the urethane and amide bands of *t*-Boc-L-Pro-Sar-OMe and *t*-Boc-Sar-Sar-OMe in TMP (not shown in the figure) at 1700–1697 and 1672–1665 cm^{-1}, respectively, are consistent with the above interpretation.

In D_2O all C=O groups are strongly solvated, as indicated by the occurrence of three bands at 1720–1715 cm^{-1} (bonded acid C=O groups),[1,34] 1657–1650 cm^{-1} (bonded tertiary urethane C=O groups),[5] and 1633–1628 cm^{-1} (bonded tertiary amide C=O groups).[34] Below 1700 cm^{-1} the spectra of *t*-Boc-L-Pro-Sar-OH and *t*-Boc-Sar-Sar-OH are almost identical with those of the corresponding methyl ester derivatives.

It may be concluded that *t*-Boc-L-Pro-Sar-OH and *t*-Boc-Sar-Sar-OH are almost completely solvated in polar solvents. In solvents of relatively low polarity ($CDCl_3$) nonaggregated and aggregated (through formation of hydrogen bonds involving exclusively the carboxyl group as hydrogen acceptor) species coexist, the extent of the latter increasing with increasing concentration. Interestingly, even in very dilute solution in $CDCl_3$ the amounts of intramolecularly hydrogen-bonded species, if any, seem to be negligible.[35]

Supplementary Material Available: Structure factor tables for *N-tert*-butyloxycarbonylsarcosylsarcosine and *N-tert*-butyloxycarbonylprolylsarcosine (22 pages). Ordering information is given on any current masthead page.

References and Notes

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(35) During the preparation of the manuscript we became aware of a paper by K. Itoh, T. Yamane, and T. Ashida, *Acta Crystallogr.*, **34**, 2640 (1978), which also describes results of an independent X-ray diffraction analysis of *t*-Boc-L-Pro-Sar-OH. We were pleased to note that the overall conformation of the molecule and the details of the geometrical parameters reported by Japanese authors match closely those described in the present paper.

Polymer Diffusion in a Dilute Solution. 2. Poly[bis(*m*-chlorophenoxy)phosphazene] in Chloroform

B. Chu* and Esin Gulari

Chemistry Department, State University of New York at Stony Brook, Long Island, New York, 11794. *Received December 11, 1978*

ABSTRACT: Translational diffusion coefficients of poly[bis(*m*-chlorophenoxy)phosphazene] of known molecular weight distribution in chloroform at 25 °C have been studied using Rayleigh line-width spectroscopy. By combining light scattering intensity measurements where we determined the molecular weight $M_r = 3.45 \times 10^6$ g/mol, the second virial coefficient $A_2 = 1.39 \times 10^{-4}$ (cm^3 mol)/g^2, and the radius of gyration $\langle r_g^2 \rangle^{1/2} = 1.54 \times 10^3$ Å with the concentration dependence of the diffusion coefficient $k_D = 116$ g of solution/g or 78.4 cm^3/g, and the molecular weight dependence of radius of gyration $r_g = 2.89 \times 10^{-9} M^{0.57}$, we are able to make a transformation from Γ space to M space and to obtain the molecular weight distribution function from a histogram analysis of the photoelectron time correlation function of light scattered by the polymer solution at a finite concentration. Our molecular weight distribution function is in essential agreement with the GPC result. It should be noted that this new approach should enable determinations of molecular weight distribution functions of extremely high molecular weights ($\sim 10^9$ g/mol), not accessible by the GPC method. Furthermore, the method is nondestructive, needs only small quantities of the polymer solution, and, in principle, takes merely minutes for each measurement and analysis under most circumstances.

I. Introduction

The high molecular weight, open-chain poly(dichlorophosphazene) obtained from high-temperature melt polymerization of hexachlorocyclotriphosphazene is a thermally stable elastomer but lacks hydrolytic stability. Allcock[1] was able to substitute the reactive chlorine groups of poly(dichlorophosphazene) with a variety of organic nucleophiles. Aside from the earlier reviews by Allcock,[2,3] the synthesis, properties, and applications of polyphosphazenes have been reported[4] and reviewed[5] by members of the Army Materials and Mechanics Research Center at Watertown, Mass. Of the seven different poly(aryloxyphosphazene) homopolymers reported,[4] the molecular weight distribution of poly[bis(*m*-chlorophenoxy)phosphazene] (sample IIIe in ref 4) has been determined using a Waters ANAPREP gel permeation chromatograph.[6] In this article, we explore a new general approach to the determination of molecular weight distribution of linear poly(phosphazenes) using a well characterized poly[bis(*m*-chlorophenoxy)phosphazene] (sample IIIe in ref 4)[7] as an example. In section II, we shall provide the theoretical background for a generalized procedure in the determination of molecular weight distribution of polymer solutions by means of light-scattering spectroscopy. In sections III and IV, the experimental methods and procedures of data analysis will be outlined. Finally, we shall illustrate this new method by presenting the light scattering results of sample IIIe.

II. Theoretical Background

A. Light-Scattering Intensity Measurements. According to the Rayleigh–Gans–Debye theory,[8] the

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