

TABLE II
 STRUCTURAL PARAMETERS FOR *t*-BUTYL CHLORIDE AND RELATED MOLECULES

Molecule, <i>t</i> -butyl	r_{C-X} , Å.	r_{C-C} , Å.	r_{C-H} , Å.	$\angle C-C-C$	$\angle C-C-H$	Method	References
Chloride	1.828	1.532	1.104	107.4°	110.0°	ED ^a	Present study
Chloride	1.803	1.530		108.1°		MW ^b	c
Chloride	1.80	1.54		107.5°		ED	4b
Chloride	1.80	1.54	1.10	107.0°		ED	4a
Chloride	1.765	1.55	1.09 (ass.)		109° 28' (ass.)	ED	5
Chloride	1.78	1.54 (ass.)	1.093 (ass.)	109° 28'	109° 28' (ass.)	MW	7
Fluoride	1.43	1.525				MW	3
Acetylene	1.495	1.532		108.11°		MW	2
Cyanide	1.495	1.532		108.42°		MW	2

^a Electron diffraction. ^b Microwave spectroscopy. ^c D. R. Lide, Jr., and M. Jen, *J. Chem. Phys.*, **38**, 1504 (1963).

4 ± 2 kcal./mole. The large uncertainty is mainly due to the fact that the amplitude of vibration for the methyl carbon to *gauche* hydrogen, on a neighboring methyl group, interaction cannot be determined with any great degree of reliability. The barrier is, however, in agreement with values reported for similar compounds.^{3,15,16}

The C-C-Cl bond angle of 107.4° found in this investigation is in excellent agreement with the results of the most recent previous electron diffraction work.^{3,4,5} The extra long C-Cl bond value has led us to consider other possible sources of error in the analysis. About the only impurity that could cause a shift in the C-Cl bond would be Cl₂, but it would take a 4.25% molar concentration of this molecule to shift an r_{C-Cl} distance of 1.806 Å. to the reported 1.828 value. This would also require an 8.5% conversion of *t*-butyl chloride to another form and it is hard to imagine how this could take place without causing observable distortions in the carbon skeleton parameters. It also does not seem that Cl₂ would, in fact, even be the most likely decomposition product under the conditions of the experiment. In summary, since all the bonded peak areas checked with the theoretical values to less than 1%, it does not appear that the present results for the C-Cl bond length could be due to the presence of an impurity.

It would seem that a simple steric argument could easily account for the observed lengthening of the C-Cl

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bond. The C-C bond lengths do not have to change appreciably as the strain imposed by the presence of the Cl is diluted somewhat among the three methyl groups, and a change in the C-C-Cl angle could account for the rest. The chlorine can only relieve the strain by moving away from the tertiary carbon atom. This change should, of course, lead to an increase in the bond moment of the C-Cl bond. It is of interest to note that regardless of what the correct interpretation of this phenomenon is, there seems to be an experimental rule of thumb that, in structures of the type considered here, the unique bond length always increases. This was shown first by Swick, *et al.*,¹⁷ in hexachloroethane, and additional evidence in support of this result has been obtained from a recent re-determination of hexachloroethane by Traetteberg.¹⁸ She has shown that the carbon-carbon bond, in this molecule, has been elongated by 0.031 Å. while the -CCl₃ groups appear to be normal except for slight angle changes.

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Electron Diffraction Determination of the Molecular Structure of the Butyl Halides. IV. The Structure and Conformational Analysis of *n*-Butyl Bromide in the Gas Phase^{1a}

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The structure and conformational analysis of gaseous *n*-butyl bromide has been carried out by the sector-microphotometer method of electron diffraction. The molecular parameters for the bonded distances were found to be: $r_g(C-H) = 1.101$ Å., $r_g(C-C) = 1.532$ Å., and $r_g(C-Br) = 1.950$ Å.; $l_m(C-H) = 0.071$ Å., $l_m(C-C) = 0.051$ Å., and $l_m(C-Br) = 0.050$ Å.; and $\angle C-C-C = 112.4^\circ$, $\angle C-C-Br = 111.0^\circ$, and $\angle C-C-H = 110.0^\circ$. The distribution of conformers at room temperature was found to be the same as the distribution for *n*-pentane. This gives identical energy differences favoring the *trans* forms at each end of the molecule by 650 cal./mole.

This work is the first attempt to obtain a complete structure determination of *n*-butyl bromide.^{2a,b} It is therefore of interest to obtain precise values of the

(1) (a) Contribution number 1079 from the Chemical Laboratories of Indiana University. (b) Indiana University. The authors wish to thank the National Science Foundation and the Atomic Energy Commission for their financial support of this work and W. H. M. wishes to thank the National Science Foundation for a Faculty Summer Research Participation Grant. (c) Youngstown University.

(2) (a) R. J. W. LeFevre, R. Roper, and A. J. Williams, *Australian J.*

bonded parameters for comparison with other similar halogen-substituted molecules. In view of the fact that both fluorine and chlorine stabilize *gauche* conformations,³⁻⁵ it is also of interest to determine to what

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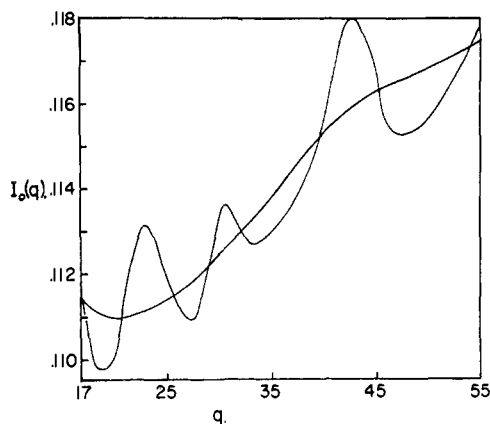


Fig. 1.—The long camera distance intensity data and the background for *n*-butyl bromide.

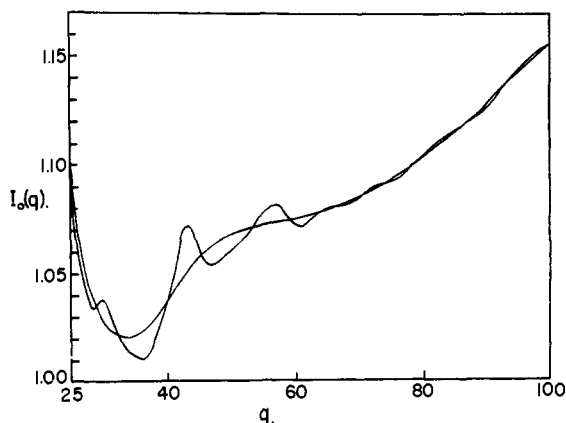


Fig. 2.—The short camera distance intensity data and the background for *n*-butyl bromide.

extent bromine influences the stability of the *gauche* forms in an *n*-butyl group. It is also of interest in bromine-containing compounds to examine the effect of the failure of the Born approximation on the scattering data.

Experimental

A sample of *n*-butyl bromide was obtained from the Columbia Chemical Co. and analyzed by gas chromatography. The boiling point and index of refraction were checked and the sample used appeared to be over 99% pure. To avoid possible decomposition, the sample was purified immediately prior to the taking of the diffraction photographs by vacuum distillation. Electron diffraction photographs were obtained with an r^3 sector using the sector electron diffraction camera in Professor L. S. Bartell's laboratory at Iowa State University. Specimen pressures of 20 to 50 mm. with exposure times of 1 to 5 sec. were used at a temperature of 298°K. The beam current was 0.39 μ a. and the accelerating voltage was 40 kv. Four research grade Kodak process photographic plates at each of two camera distances were obtained for each molecule. Plates were selected which contained no visually observed flaws. The photographic plates were microphotometered in Professor L. O. Brockway's laboratory at the University of Michigan.

The microphotometer traces of the electron diffraction photographs were read at 0.25-mm. intervals, to four significant figures, with the aid of a Bausch and Lomb 7-power measuring magnifier. The photographic emulsion was calibrated by a procedure developed by Bartell and Brockway.⁶ The indices of resolution for the 21.35-cm. camera distance were found to be 0.90 and for the 10.66-cm. distance, 1.00. It was felt that the near unity values of the indices indicated the absence of any serious extraneous scattering effects.

Structural Analysis.—The experimental data were analyzed according to schemes outlined elsewhere.⁷⁻⁹ Bond lengths, vibrational amplitudes, and information on hindered rotation

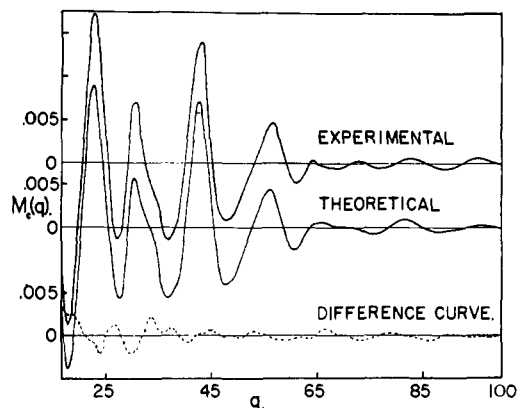


Fig. 3.—The experimental and theoretical reduced molecular intensity curves and their difference.

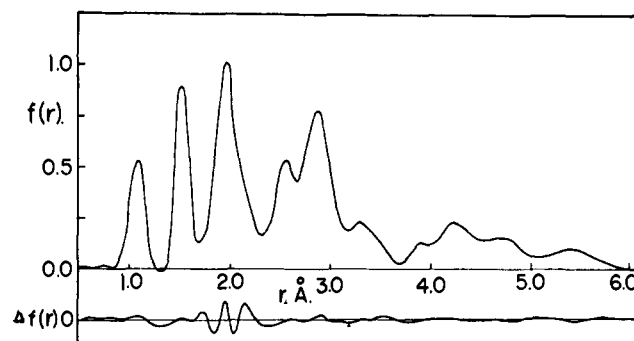


Fig. 4.—The experimental radial distribution curve and the difference, $\Delta f(r)$, between it and the best theoretical model.

were all obtained by least squares analysis of the radial distribution curve. Corrections for electron-electron scattering, failure of the Born approximation,¹⁰ asymmetry of vibration for bonded distances, and Fourier integral termination errors were all applied. The calculated experimental radial distribution curve made use of experimental data, at integral q -values, from $q = 12$ to $q = 100$. An artificial convergence factor, e^{-dq^2} , was employed where d was chosen so that the experimental value at $q = 100$ was reduced to a tenth of its value.

In order to make the analysis of the data tractable, it was assumed that all methyl groups were equivalent and that all methylene groups were equivalent. Furthermore, the terminal methyl and $-\text{CH}_2\text{Br}$ groups were assumed to exist in staggered configurations and the $\angle \text{C}-\text{C}-\text{H}$ and $\angle \text{C}-\text{C}-\text{C}$ angles were assumed to have the values found in *n*-butane.¹¹ It was possible to check the assumptions in the case of the $\angle \text{C}-\text{C}-\text{H}$ and $\angle \text{C}-\text{C}-\text{C}$ angles since rough estimates can be obtained for these parameters from consideration of some of the longer and better resolved non-bonded peaks in the radial distribution curve. An ethane-like barrier was assumed to exist about each carbon-carbon bond so that the molecular structure at room temperature could be described in terms of a mixture of conformers as in the case of *n*-butyl chloride.⁴ Also, the bonded C-C and C-H distances reported in this investigation are average values of what might be unequivalent distances. Previous work has indicated that C-C distances tend to be constant throughout the molecule to within the experimental error while C-H distances tend to increase somewhat as the number of methylene groups increase in proportion to the number of methyl groups.¹²

In the conformational analysis, *gauche* angles were initially assumed to be 60° but were later adjusted to 67° to fit the data. A *trans* angle of 180° was also assumed. The percentage of each conformer present at room temperature was determined by fitting the intensity data and radial distribution curves with a linear combination of the curves for the pure conformeric forms. The curves for the pure forms were computed using all the experimental data obtained in the analysis of the rigid framework parameters from the radial distribution curve and the necessary assumed parameters discussed above.

Results

Figures 1 and 2 show the experimental long and short camera distance intensity curves and the corresponding

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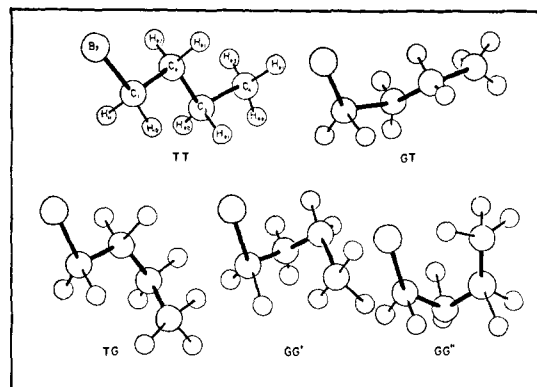
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TABLE I

MOLECULAR PARAMETERS AND THEIR UNCERTAINTIES FOR *n*-BUTYL BROMIDE

Peak	$r_k(0)$	δr	$l_{ij, \text{exp.}}$	δl_{ij}
C-H	1.101	± 0.006	0.071	± 0.008
C-C	1.532	± 0.004	.051	± 0.007
C-Br	1.950	± 0.010	.050	± 0.010
C-H	2.183	± 0.010	.110	± 0.010
C-C	2.544	± 0.010	.070	± 0.010
Br-C _{gauche}	3.330	± 0.015	.080	± 0.015
C-C _{trans}	3.920	± 0.015	.090	± 0.015
Br-C _{trans}	4.275	± 0.020	.100	± 0.020
Br-C _{trans}	5.415	± 0.025	.125	± 0.025
$\angle \text{C-C-C}$	$112.4 \pm 1.0^\circ$			
$\angle \text{Cl-C-C}$	$111.0 \pm 1.0^\circ$			
$\angle \text{C-C-H}$	$110.0 \pm 1.5^\circ$			

background functions. In Fig. 3, the experimental and theoretical $M(q)$ curves and their difference are presented. The agreement between theory and ex-

Fig. 5.—Possible conformeric forms of *n*-butyl bromide.

perimental requirements because the Br-H distance would have to be 1.8 Å., which should be too short to allow the existence of this species without a serious distortion

TABLE II

STRUCTURAL PARAMETERS FOR *n*-BUTYL BROMIDE AND RELATED COMPOUNDS

Molecule	$r_{\text{C-Br}}$, Å.	$r_{\text{C-C}}$, Å.	$r_{\text{C-H}}$, Å.	$\angle \text{C-C-C}$	$\angle \text{C-C-Br}$	Method	Reference
<i>n</i> -Butyl bromide	1.950	1.531	1.101	112.4°	111.0°	SMED ^a	Present study
<i>n</i> -Butane		1.533	1.103	112.5°		SMED	11
<i>n</i> -Butyl chloride		1.533	1.110	112.1°		SMED	4
Allyl bromide	1.94	1.53		108.9°		SMED ^a	d
Ethyl bromide	1.940				110.5°	MW ^b	e
Bromopicrin	1.92					SMED ^a	f
Ethyl bromide	1.950	1.518	1.087		$111^\circ 2'$	MW	14
	% of conformers ^c	<i>n</i> -Butyl bromide	<i>n</i> -Butyl chloride	<i>sec</i> -Butyl chloride	<i>n</i> -Pentane	<i>n</i> -Propyl chloride	
	TT	36	11		42.6		
	TG	24	11	25	25.0	20	
	GT	24	37	48	25.0	80	
	GG'	16	17	27	7.3		
	GG''		24				

^a Sector microphotometer method of diffraction. ^b Microwave spectroscopy. ^c First symbol refers to halogen. ^d H. J. M. Bowen, A. Gilchrist, and L. E. Sutton, *Trans. Faraday Soc.*, **51**, 1341 (1955). ^e R. S. Wagner, N. Solimene, and B. P. Daily, *J. Chem. Phys.*, **23**, 599 (1955). ^f I. L. Karle and J. Karle, *ibid.*, **36**, 1969 (1962).

periment in the region $65 \leq q \leq 100$ is remarkable considering the absolute value of the $M(q)$ functions in this region. This agreement would seem to indicate that the phase shifts $\eta_i(s)$ ¹³ given by Hoerni and Ibers are in excellent agreement with experiment. Figure 4 shows the experimental radial distribution curve and the difference between it and the curve for the best theoretical model. The large deviations in the vicinity of the C-Br peak are due to the fact that the analytical expressions for the $\eta_i(s)$ phase shifts¹⁰ are incorrect for $s > 60$. The Fourier transform of the reduced intensity $M(q)$ containing these $\eta_i(s)$ functions will be incorrect unless a suitable damping factor is employed. The damping factor used in Fig. 4 is not the most suitable one for the purposes of least squares analysis but has the visual advantage of possessing fairly well separated peaks.

The results of the least squares analysis for the bond distances and root mean square amplitudes of vibration are presented in Table I. The estimated uncertainties were computed using techniques described elsewhere.⁸ These estimates do not include possible sources of error due to the use of the simple kinematic scattering theory. A comparison of the results found by this investigation and with previous results for similar molecules is presented in Table II.

The possible conformers for *n*-butyl bromide are shown in Fig. 5. The GG'' conformer was ruled out by

of the rest of the molecule. A least squares fit of the intensity data with a linear combination of conformers, including the GG'' form, also indicated the absence of the GG'' conformer. The results of the least squares fits of the intensity and radial distribution curves gave conformer percentages nearly identical with those found for *n*-pentane.¹² The percentage of *trans* conformer at each end was found to be 60% and the *gauche* conformer, 40%. The free energy change, ΔF° , for the reaction $T \rightleftharpoons G$ at each end of the molecule was found to be 650 ± 150 cal. at 300°K. In the above analysis, it was assumed that there was no coupling between barriers on adjacent C-C bonds.

The parameters determined for the $r_g(\text{C-C})$, $r_g(\text{C-H})$, $r_g(\text{C-Br})$, and $\angle \text{C-C-Br}$ in this work are in excellent agreement with the microwave results for ethyl bromide¹⁴ as indicated in Table II. It would appear that the configuration of the CH₂Br group is not appreciably changed by substitution of an ethyl group for a hydrogen atom on the neighboring carbon atom. The failure of the Br, in this case, to stabilize the *gauche* conformation is of particular interest. This observation is probably in keeping with the idea that *gauche* stabilization may be a result of nonbonded electrostatic interactions¹⁵ since the Br atom has an electronegativity similar to that of carbon on the Pauling scale and as a result might be expected to exhibit behavior not unlike that of a methyl group.

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Acknowledgments.—The authors wish to thank Dr. T. Ukaji for his help in reading the traces. We also thank Professor L. S. Bartell for the use of his diffraction apparatus at Iowa State University and Professor L. O. Brockway for the use of his recording micro-

photometer at the University of Michigan. We gratefully acknowledged the Indiana University Research Computing Center for the use of their IBM 709 digital computer, and Mrs. Connie Williams for her help in the preparation of the manuscript.

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Infrared Spectra of Aqueous Solutions. IV. Glycine and Glycine Peptides¹

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Infrared spectra of glycine and glycine peptides have been measured at various pD values in aqueous solutions. On the basis of the antisymmetric stretching frequencies of the ionized and un-ionized carboxyl groups, and the frequency changes of the peptide carbonyl groups as a function of solution acidity, the structures of the free ligands are inferred. Ionization constants are determined from the plots of the absorbancy vs. $-\log [D^+]$ and are compared with the results of potentiometric studies. All optical measurements have been made at 20° and at an ionic strength adjusted to 1.0 *M* with KCl. Potentiometric titrations have been made at ionic strengths of 1.0 *M* (KCl) and 0.1 *M* (KNO₃).

Introduction

Before undertaking an infrared study of the structures of metal chelates formed from peptides in solution, it is necessary to determine the infrared spectra of the various free ligand species present in solution. As has been shown by previous workers,²⁻⁴ it is possible to detect the cationic, neutral, dipolar, and anionic species of amino acids in aqueous solutions by measurement of the infrared carboxyl group absorption as a function of pD. In this paper the infrared technique is extended to a determination of the structures of glycine peptides in aqueous solution. The dissociation constants obtained from spectral (infrared) measurements will be compared to the dissociation constants determined potentiometrically under the same conditions, so that the microscopic information obtained from infrared spectra can be applied to the extensive potentiometric investigations previously reported in the literature.⁵ Values of dissociation constants in D₂O will also be available for comparison with the corresponding values previously obtained in H₂O.

Experimental

Spectral Measurements.—Infrared spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer fitted with sodium chloride optics. Silver chloride absorption cells of 0.0165 mm. thickness were employed. The concentrations of ligand solutions were 0.2–0.6 *M* in 99.8% D₂O as solvent, purchased from Bio-Rad Lab., Richmond, Calif. The wave numbers reported are accurate to ± 3 cm.⁻¹. The ionic strengths of all the solutions were adjusted to 1 *M* by adding reagent grade potassium chloride which was shown to have no absorption in the range of frequencies investigated. Deuterium ion concentrations were measured with a Beckman model G pH meter fitted with extension glass and calomel electrodes of the special "one-drop" type and calibrated at 20° in the same way as is described below for potentiometric measurements. Calibration of the D₂O–pH meter electrode system was made by titration of a strong acid (DCl) and a strong base (NaOD), as well as a weak acid (acetic acid, DC₂H₃O₂) under the conditions employed for the infrared measurements. The DCl solution employed to adjust pD in D₂O was obtained from concentrated hydrochloric acid by dilution with D₂O, and the sodium deuterioxide (NaOD) solution was prepared by dissolving sodium metal in D₂O. Two sample solutions of the same ligand concentration and the same ionic strength, but of different pD (one very high, the other very low), were mixed to prepare samples having the desired pD values.

(1) This investigation was supported by research grant AM-06019-0152 from the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

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Potentiometric Measurements.—The method employed is the same as reported by others.^{6,7} Measurements were made under three different reaction conditions: a, 0.1 *M* ionic strength adjusted with KNO₃ at 25°; b, 1.0 *M* ionic strength adjusted with KCl at 25°; and c, 1.0 *M* ionic strength adjusted with KCl at 20° in D₂O solvent. The results obtained under these conditions were compared with the results of the spectral studies. The concentration of the ligands were 0.001–0.0015 *M*.

Compounds.—Glycine was purchased from the Fisher Scientific Co., Fair Lawn, N. J.; glycyglycine was obtained from California Biochemical Research, Los Angeles, Calif.; triglycine and pentaglycine were purchased from Mann Research Lab., New York, N. Y.; and tetraglycine was obtained from the Nutritional Biochemicals Corp., Cleveland, Ohio. Glycine, glycyglycine, and tetraglycine were recrystallized two times from aqueous alcohol solutions. Tetraglycine was analyzed by the Micro-Tech Lab., Skokie, Ill. Other compounds were used without recrystallization. Before the solutions were prepared, the compounds were dried carefully at 110° and cooled in a desiccator over P₂O₅. The triglycine employed was specified to be chromatographically pure grade.

Results

Glycine.—The infrared spectra of aqueous glycine at four deuterium ion concentrations are given in Fig. 1. The frequencies of the absorption maxima correspond-

TABLE I
ANTISYMMETRIC CARBOXYL AND PEPTIDE CARBONYL BANDS OF
GLYCINE AND GLYCINE PEPTIDES AS A FUNCTION OF pD

Ligand	pD	Observed bands, cm. ⁻¹			Probable species
		COOH (N ⁺)—COO ^{-a}	COO ^{-a}	COO ⁻	
G	A 1.54	1732vs	1617w	I and IIa
	B 4.84	1617vs	IIa
	C 9.74	1618vs	1580m	IIa and III
	D 10.61	1616m	1580vs	IIa and III
GG	A 1.75	1720m	1675vs	I
	B 4.31	1720vw	1675vs	1595vs I and IIa
	C 8.77	1665m	1630w	1595vs IIa and III
	D 10.29	1632m	1595vs III
	GGG	A 1.31	1723m	1678vs	1656s
B 3.77		1724w	1678vs	1653s	1597s I and IIa
C 5.67		1678vs	1648s	1597vs IIa and III
D 10.16		1644vs	1597vs III
GGGG	A 1.20	1722m	1675 ^c	1658vs ^c I
	B 3.68	1725w	1670 ^c	1650vs ^c	1597m I and IIa
	C 6.70	1673 ^c	1648vs ^c	1596vs IIa and III
	D 12.74	1643vs	1597vs III

^a (N⁺)—COO⁻ indicates the band due to dipolar structure while COO⁻ indicates the band due to anionic structure. ^b Peptide carbonyl group; (N⁺)—CO represents carbonyl band with positive α -nitrogen atom, (N)—CO represents carbonyl band with neutral α -nitrogen atom. ^c Broad band observed since constituent bands not resolvable.

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