since the semipolar bond to oxygen, putting a positive charge on the sulfur, would greatly increase its electron affinity, thereby causing an induced positive charge on the ring. The fact that this charge is essentially equal in the *m*- and *p*-positions (as indicated by the σ-constant) is in agreement with the very small estimated polarizing force for the sulfoxide group of -0.01×10^{-4} dyne.[22]

The ultraviolet absorption data in Table I indicate that the remaining unshared electron pair on the sulfoxide still retains strong conjugative properties, though definitely less than for the sulfide group.

The σ-constants for the sulfone group (σ_p = 0.76 and σ_m = 0.65) are more positive as expected because of a stronger inductive effect of the more positive sulfur atom in the sulfone. The difference in σ-constants is qualitatively in accord with expectation based on the calculated polarizing force of $+1.55 \times 10^{-4}$ dyne.[22]

The utilization in bonds with oxygen of both the electron pairs of the sulfur which were unshared in the sulfide has a marked effect in diminishing the conjugation properties of the sulfonyl group with the carbethoxyl group, especially evident in the marked increase in the absorption coefficient for the maxima around 280 mμ.

NOTRE DAME, INDIANA RECEIVED JULY 11, 1951

[CONTRIBUTION FROM THE CHILDREN'S CANCER RESEARCH FOUNDATION AND THE DIVISION OF LABORATORIES AND RESEARCH OF THE CHILDREN'S MEDICAL CENTER, AND THE DEPARTMENT OF PATHOLOGY, HARVARD MEDICAL SCHOOL AND FROM THE LABORATORIES OF THE POLAROID CORPORATION AND THE AMERICAN OPTICAL COMPANY]

Infrared Spectra and the Structure of Glycine and Leucine Peptides[1]

BY ELKAN R. BLOUT AND SEYMOUR G. LINSLEY

The infrared spectra of a series of glycine homopeptides and glycine–leucine heteropeptides have been measured in the solid state over the spectral range 650–4000 cm.$^{-1}$. The spectra of the glycine homopeptides show no evidence of unassociated amino groups, and in such peptides having varying molecular weights there is evidence of strong hydrogen bonding. There is a band in the spectra of these compounds at 1015 ± 10 cm.$^{-1}$ which appears to be characteristic of the diglycyl grouping. In some of the glycine–leucine heteropeptides there are apparently unassociated amino groups. In both the glycine peptides and the glycine–leucine peptides in the solid state there are both ionized and non-ionized carboxyl groups, as indicated by absorption bands at 1400 and 1680 cm.$^{-1}$, respectively. There is an unassigned absorption band about 700 cm.$^{-1}$ which appears in the spectra of all peptides and proteins examined.

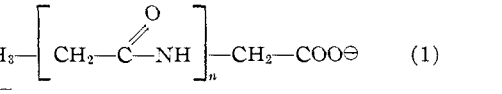
Recently several groups of workers have reported on some applications of infrared spectroscopy to the determination of the molecular structures of polypeptides and proteins.[2] In our laboratory we are investigating the effects of molecular weight and chemical constitution of polypeptides on their infrared spectra and the relationships that exist in the infrared spectra of amino acids, peptides, polypeptides and proteins. In this communication we report work with peptides and polypeptides of glycine and leucine.

The Glycine Peptides—In order to better interpret the infrared spectral data obtainable from high molecular weight polypeptides and proteins composed of many different amino acids, it was felt that it would be valuable to examine the spectra of a series of simple peptides. Consequently, we have determined the spectra of a homologous series of peptides of glycine, the most simple amino acid. Figure 1 shows the infrared spectra of glycine, diglycine, triglycine, tetraglycine, pentaglycine, hexaglycine and polyglycine[3] measured in the solid state over the spectral region 650 to 3600 cm.$^{-1}$ (approximately 2.75 to 15.3 microns).

Several observations may be made from an examination of these spectra: (1) As the molecular weight of the glycine peptide increases beyond triglycine, the spectra show fewer distinct absorption bands, and in the main outline the polyglycine spectrum approximates to that obtained with proteins such as histone and ribonuclease.[4]

(2) The strongest absorption bands in all the spectra are those associated with N–H stretching ($\sim$ 3300 cm.$^{-1}$), C=O stretching ($\sim$ 1650 cm.$^{-1}$) and amide N–H deformation ($\sim$ 1540 cm.$^{-1}$). Also there is a prominent, but not quite as strong band occurring around 1440 cm.$^{-1}$ which presumably is a CH_2 deformation mode.

(3) There is a very strong band at 1400 cm.$^{-1}$ in the spectra of glycine and di-, tri- and tetraglycine. This band becomes less intense in penta- and hexaglycine until in the polyglycine sample the band appears only as an inflection point. It may be assumed that this band is caused by ionized carboxyl groups from dipolar or zwitter ion forms such as I, especially since it would be expected that



(1)

(1) Presented in part at the Symposium on the Infrared Spectra of Large Molecules, 119th Meeting of the American Chemical Society, Boston, Massachusetts, April, 1951. This work was supported in part by U. S. Public Health Service Grant C-1522.

(2) See, for example, (a) W. T. Astbury, C. E. Dalgliesh, S. E. Darmon and G. B. B. M. Sutherland, *Nature*, **162**, 596 (1948); (b) E. J. Ambrose, A. Elliott and R. B. Temple, *ibid.*, **163**, 859 (1949); (c) I. M. Klotz, P. Griswold and D. M. Gruen, THIS JOURNAL, **71**, 1615 (1949); (d) S. E. Darmon and G. B. B. M. Sutherland, *Nature*, **164**, 440 (1949); (e) L. L. Uzman and E. R. Blout, *ibid.*, **166**, 862 (1950); (f) E. J. Ambrose and A. Elliott, *Proc. Roy. Soc.* (*London*), **A205**, 47 (1951).

(3) The spectrum of polyglycine from 700 to 1650 cm.$^{-1}$ reported previously by Sutherland, *et al.* (ref. 1a), and our results in this region are in substantial agreement. After this work was completed and while this manuscript was in preparation an article by H. W. Thompson, D. L. Nicholson and L. N. Short appeared in Spectroscopy and Molecular Structure, *Discussions of the Faraday Society*, **9**, 222 (1950). In this article there appeared some data over a more limited spectral range for a few of the compounds reported in this communication.

(4) E. R. Blout and R. C. Mellors, *Science*, **110**, 137 (1949).

contributions from structures such as this would decrease with increasing n. Also Edsall and his coworkers[5,6] have shown that the Raman spectra of glycine, diglycine and other amino acids show an intense frequency about 1400 cm.$^{-1}$ which is characteristic of an ionized carboxyl group.

Worth noting is a relatively weak band at 1680 cm.$^{-1}$ in the lower glycine peptides which appears only as an inflection point in the polyglycine spectrum. This band may be explained as due to C=O of non-ionized carboxyl, and is not present in glycine since in the crystalline state glycine exists completely in the dipolar form.[7] It is diminished in intensity in polyglycine because of its lower concentration relative to the peptide linkages. This band at 1680 cm.$^{-1}$ may be related to a band at 1305 cm.$^{-1}$ which is not seen in the glycine spectrum but is shown by the other glycyl peptides although again only as an inflection point in polyglycine.

(4) In the lower frequency region, there is an absorption band around 700 cm.$^{-1}$ which is shown by each glycine peptide as well as by the co-peptides of glycine and leucine (*cf.* Figs. 3, 4, 5, 6).

(5) Finally mention should be made of a strong absorption band at 1015 ± 10 cm.$^{-1}$ which appears in the spectra of all the simple glycine peptides examined. It would seem that this band represents a skeletal vibration of a portion of the unsubstituted peptide chain since it is also appears in polyglycine methyl ester, but does not appear in poly-L-leucine, or in poly-L-alanine,[2] but is observed in certain glycine–leucine copeptides (*vide infra*).

Referring now to the spectral region around 3000 cm.$^{-1}$, in Fig. 2 there is shown the data for well-dried samples of di-, tri-, tetra-, penta-, hexa- and polyglycine with optical density plotted as a function of frequency. These samples were prepared as finely ground hexachlorobutadiene mulls of the solid materials and the thicknesses were adjusted to optical densities between 0.6 and 1.1 in the 3300 cm.$^{-1}$ band. The spectra in this region are characterized by four main absorption bands, *viz.*, bonded N–H (a) 3300 cm.$^{-1}$, bonded N–H (b) 3080 cm.$^{-1}$, non-symmetrical C–H stretching of CH_2 2925 cm.$^{-1}$ and symmetrical C–H stretching of CH_2 2860 cm.$^{-1}$. In order to show the intensity changes which occur in the hydrogen bonded N–H band (a), at 3300 cm.$^{-1}$, all the curves were plotted on semi-log paper and the band (b) at 3080 cm.$^{-1}$ was equilibrated to density 0.3 in a manner similar to that previously described.[2e] It may be seen (Fig. 2) that there is a large and almost regular stepwise increase in the intensity of the 3300 cm.$^{-1}$ maximum as the molecular weight of the glycine peptides is increased. The only reversal of this trend occurs with hexaglycine and here the change is small. We have also plotted the data equilibrating the 2925 cm.$^{-1}$ CH band and obtained essentially the same results. Undoubtedly, the band (a) at 3300 cm.$^{-1}$ is a hydrogen bonded N–H as has been suggested by others for monosubstituted amides[8] but whether it is due only to *inter*molecular hydrogen bonds and whether the band at 3080 *cm.*$^{-1}$ is due to *intra*molecular bonds is a question that cannot be definitively answered at this time, although it is hoped that experiments now underway with simple model amides will prove fruitful. In any case, there is no question but that in the solid state the glycine peptides are highly and probably completely hydrogen bonded through the amide groups. In no glycine homopeptide is there any evidence of an absorption band in the region where unbonded N–H is usually observed (3325–3525 cm.$^{-1}$).

The binding of water vapor by glycine peptides has been studied by Mellon, Korn and Hoover[9] and they have found complete lack of water vapor absorption in di- and triglycine but tetra-, penta- and hexaglycine show very definite water vapor absorption. Comparison of the infrared absorption spectra of carefully dried samples of these peptides with the spectra of glycine peptides which had been exposed to 81% relative humidity for at least two weeks showed no change in location of the absorption bands in the region 2500 to 4000 cm.$^{-1}$ except that in the hydrated peptides an inflection point was observed at 3500 cm.$^{-1}$ which presumably is caused by bound water. There was, however, in the spectra of all the hydrated glycine peptides a noticeable increase in the intensity of the N–H absorption bands at 3300 and 3080 cm.$^{-1}$ compared with the C–H band at 2925 cm.$^{-1}$. Whether this increased absorption intensity proves to be a useful criterion in determinations of the state of hydration of proteins remains to be ascertained.

Glycyl–leucyl Dipeptides.—There are four possible dipeptides obtainable from glycine and L-leucine and their infrared spectra are shown in Fig. 3. The dipeptides show intense absorption in the 3080 cm.$^{-1}$ band except for L-leucylglycine which compound shows absorption bands at 3400 and 3510 cm.$^{-1}$. Each leucine-containing dipeptide shows a distinct band at 1680 cm.$^{-1}$ possibly indicating a larger contribution of non-ionized carboxyl groups than occurs in the glycyl peptides. In accord with the previous discussion each dipeptide shows an absorption band at 1400 cm.$^{-1}$ and a weaker band at 700 cm.$^{-1}$. It is interesting to note that the 1400 cm.$^{-1}$ band of glycyl-L-leucine is somewhat weaker than in the other dipeptides, but both the 1305 cm.$^{-1}$ and the 1680 cm.$^{-1}$ bands are stronger than in related compounds. In addition to the dipeptides shown in Fig. 3, the spectra of glycyl-D-leucine and D-leucylglycine have been determined and found to be identical to that of their corresponding optical isomers.

Glycyl–leucyl Tripeptides.—The infrared spectra of the tripeptides of glycine and leucine are shown in Fig. 4. Again in contrast to the homopeptides of glycine, the mixed peptides frequently show absorption bands in the region 3400–3550 cm.$^{-1}$. The spectrum of L-leucylglycylglycine has also

(5) J. T. Edsall and H. Scheinberg, *J. Chem. Phys.*, **8**, 520 (1940).

(6) J. T. Edsall, J. W. Otvos and A. Rich, THIS JOURNAL, **72**, 474 (1950).

(7) G. Albrecht and R. B. Corey, *ibid.*, **61**, 1087 (1939).

(8) R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1248 (1947).

(9) E. F. Mellon, A. H. Korn and S. R. Hoover, THIS JOURNAL, **70**, 3040 (1948).

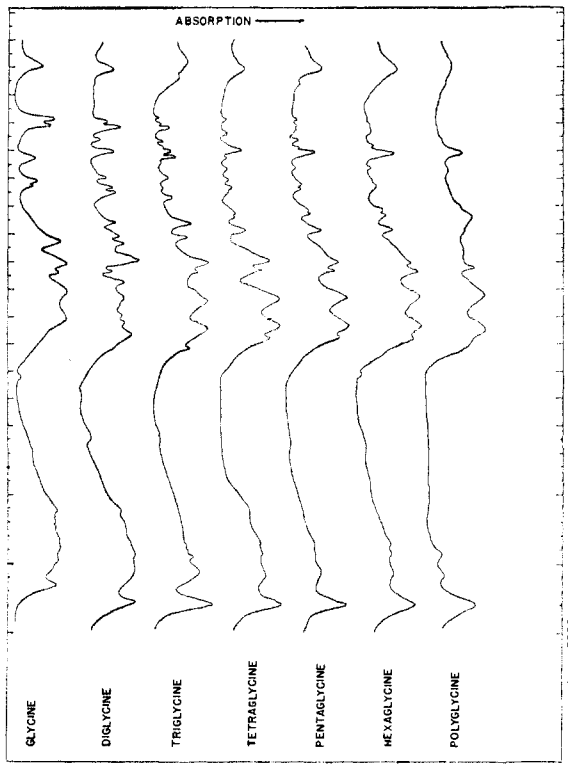


Fig. 1.—The infrared spectra of glycine and its homopeptides. All samples measured in the solid state as mulls.

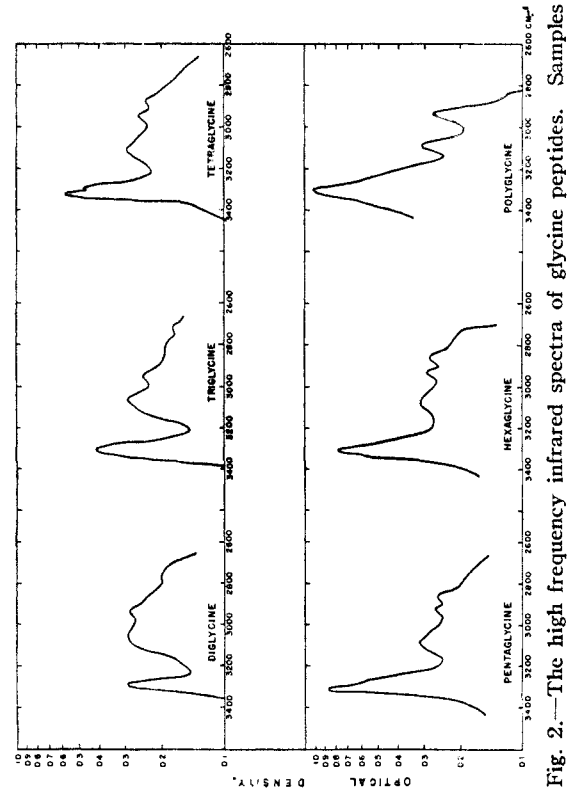


Fig. 2.—The high frequency infrared spectra of glycine peptides. Samples were measured as mulls in hexachlorobutadiene.

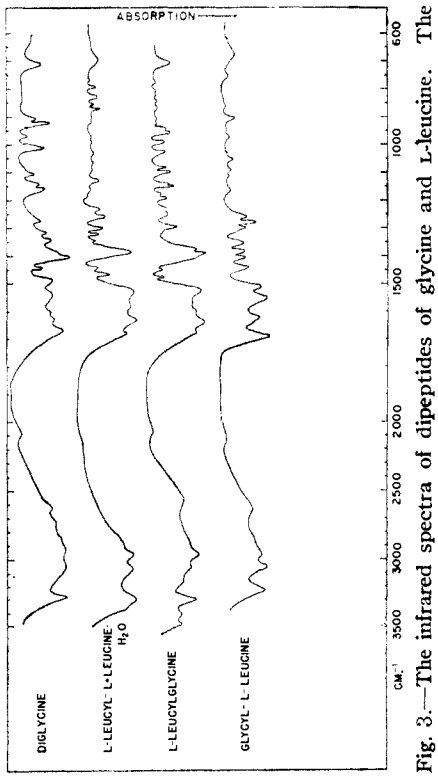


Fig. 3.—The infrared spectra of dipeptides of glycine and L-leucine. The samples were measured in the solid state as mulls.

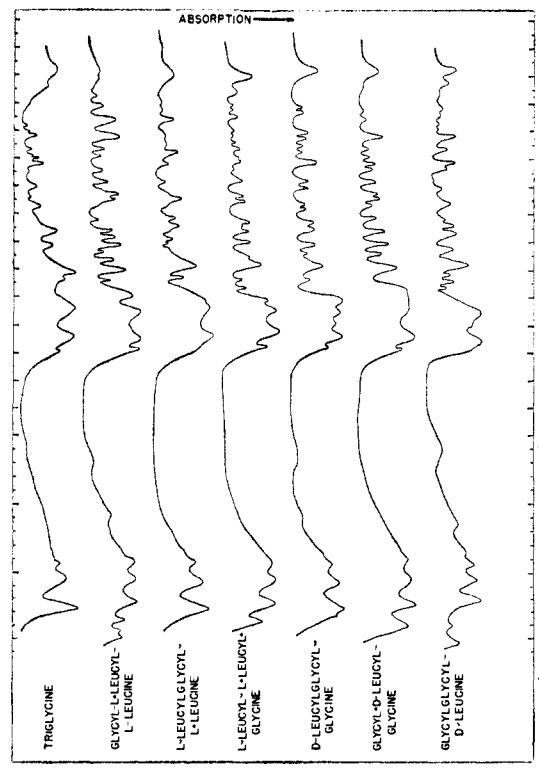


Fig. 4.—The infrared spectra of tripeptides of glycine and leucine. The samples were measured in the solid state as mulls.

been determined and found to be identical with the D-isomer. Many of the same considerations referred to previously apply to the tripeptides. There does not appear to be any correlation between the presence of bands at frequencies higher than 3300 cm.$^{-1}$ and the presence or intensity of the band around 1680–1700 cm.$^{-1}$ presumably due to on-ionized carbonxyl. It is interesting to note that in the hetero-tripeptides not only are the number of bands in the region 1525–1650 cm.$^{-1}$ variable but also their intensity and location. It is possible that this region may prove quite interesting and yield much information concerning the type of bonding in the more complicated peptides.

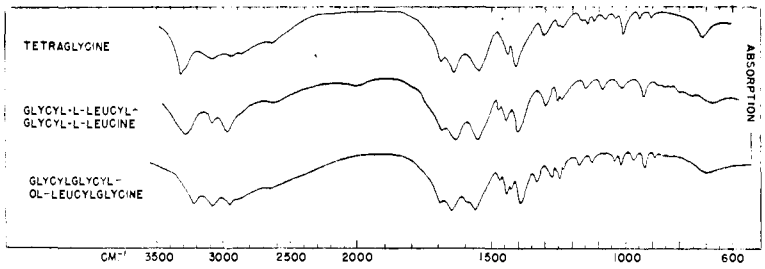


Fig. 5.—The infrared spectra of tetrapeptides of glycine and leucine. The samples were measured in the solid state as mulls.

Glycyl-leucyl Tetrapeptides.—The available higher peptides of glycine and leucine are shown in Fig. 5. The most obvious characteristic of this group is that the multibanded spectrum around 1530–1680 cm.$^{-1}$ seems to be disappearing with increasing molecular weight and beginning to dominate this region are the two main absorption bands at 1540 and 1650 cm.$^{-1}$ characteristic of the glycine peptides, other high molecular weight polypeptides, and the proteins.

Polypeptides.—In Fig. 6 there are shown the infrared spectra of polyglycine, polyglycine methyl ester and poly-L-leucine as well as triglycine methyl ester. The polypeptides all show the characteristic bands about 3300, 3080, 1650, 1540 and 700 cm.$^{-1}$. The methyl esters show a band at 1290 and 910 cm.$^{-1}$ not observed in the other glycine polymers. All the glycine compounds have a characteristic strong absorption band at 1015 ± 10 cm.$^{-1}$ but in polyglycine methyl ester it appears as a doublet. The poly-L-leucine spectrum shows, in contrast to the polyglycine spectrum, many weak absorption bands between 1200 and 700 cm.$^{-1}$. Whether this is due to presence of compounds of varying molecular weight or to complexities in the spectra caused by the hydrocarbon side chains, only further work will reveal.

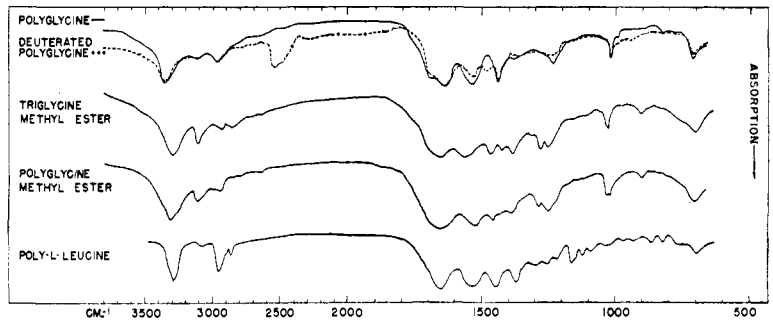


Fig. 6.—Infrared spectra: triglycine methyl ester and polyglycine methyl ester were measured as mulled samples. Polyglycine and deuterated polyglycine were measured as films cast from dichloroacetic acid solution upon silver chloride plates. The poly-L-leucine was measured as a film cast from benzene solution, and as a mulled sample.

Discussion

From the spectra of the peptides described herein several conclusions may be drawn concerning the molecular structure of these compounds. All the glycine homopeptides when examined as dry solids show two bands in the region 3000–3320 cm.$^{-1}$ and no absorption bands in the region 3320–3600 cm.$^{-1}$. The lack of absorption in the glycine homopeptides at frequencies higher than 3320 cm.$^{-1}$ certainly is indicative of the absence of unassociated $-NH_2$ groups or unassociated –OH groups. On the other hand many of the glycine–leucine peptides show absorption bands at frequencies higher than 3320 cm.$^{-1}$. Presumably these frequencies represent non-associated N–H stretching vibrations, since usually they occur at 3400 and 3520 cm.$^{-1}$ where non-symmetrical and symmetrical unassociated NH_2 vibrations of unsubstituted amides characteristically absorb in dilute solution.[8] An obvious explanation is that in the solid state the molecular packing in some of the heteropeptides is such that many of the terminal $-NH_2$ groups occupy positions where hydrogen bonding is not favored and hence the higher frequency bands appear. Since in the glycine homopeptides there are no bulky side groups, there is a much greater chance for any terminal $-NH_2$ groups to be associated with oxygen giving rise to hydrogen-bonded N–H bands. The possibility that the bands above 3300 cm.$^{-1}$ are overtones of bands around 1700 cm.$^{-1}$ has been considered but this does not seem likely in view of the intensity shown by some of these absorptions.

The bands around 3300 and 3080 cm.$^{-1}$ which presumably are related to hydrogen bonded N–H stretching vibrations seem to vary in their absorbence or density as the molecular weight of the peptide is increased. Specifically, the higher frequency band (a) at 3300 cm.$^{-1}$ shows increased absorbence (relative to either the band (b) at 3080 cm.$^{-1}$ or to the CH band at 2925 cm.$^{-1}$) with increased molecular weight of the glycine homopeptide. Possibly explanations for the increased absorbence are: (a) increased molecular extinction coefficient with increased number of peptide groups per molecule *or* (b) increased –NH hydrogen bonding in the higher molecular weight compounds. If this band at 3300 cm.$^{-1}$ is due to hydrogen bonded –NH of amide linkages, then it would be expected that the ratio of optical density of this band to that of a –CH stretching frequency would increase with the increasing number of peptide groups per molecule provided that both absorption bands obeyed Beer's law. It would be expected also that the ratio of densities would not increase indefinitely but would approach a limiting value when the number of C–H groupings approximated the number of amide groups. Our data indicate that this is the case.

We may therefore conclude that all the glycine homopeptides have essentially completely hydrogen bonded amide groups. These infrared measurements would fit in with model polypeptide structures recently proposed,[2f,10] *e.g.*, α- or β-fold or

(10) L. Pauling and R. B. Corey, THIS JOURNAL, **72**, 5349 (1950).

spiral, provided that such structures contain completely hydrogen bonded amides. In the heteropeptides, however, the infrared spectra certainly indicate that some of the NH_2 and perhaps some of the amide groups are not hydrogen bonded.

As indicated previously the absorption band at 3080 cm.$^{-1}$ does not vary in relative intensity (compared to that of C–H) with increasing molecular weight. That this band is indeed a hydrogenic frequency is indicated by the results of deuteration of polyglycine by exchange with D_2O (Fig. 6) in which there is both a decrease in intensity of this band compared to the non-deuterated polypeptide and the appearance of two new bands at 2530 and 2480 cm.$^{-1}$. These latter bands (N–D vibrations) lie close to the theoretical frequencies. We have noted that the 3080 cm.$^{-1}$ band is invariably present in all peptides and proteins examined by us, but with the limited information now available on model compounds, it seems premature to speculate now on its precise origin and significance, although one must certainly consider the possibility of its arising at least in part from $-NH_3^+$.

In all the peptides there is a very strong band present in the region 1600 to 1660 cm.$^{-1}$ (C=O stretch) and one which is usually slightly less intense in the region 1520 to 1560 cm.$^{-1}$. These absorption bands are characteristic of all linear peptides and proteins.[2] Subsidiary bands in the lower molecular weight peptides observed between 1500 and 1650 cm.$^{-1}$ are not yet readily explicable in terms of molecular structure. There is however, a noteworthy subsidiary band generally located between 1670 and 1700 cm.$^{-1}$. This band lies in the same region as do strong bands of non-ionized carboxyl groups of other types of compounds, and in the peptides presumably is also caused by such groups. In this connection, it should be noted that crystalline glycine, which from X-ray measurements appears to exist completely in the dipolar ionized form, shows no absorption band in this region.

Two additional bands shown by all the peptides are those in the neighborhood of 1440 and 1400 cm.$^{-1}$. The 1440 cm.$^{-1}$ is certainly a C–H deformation frequency but the wide intensity variations observed are puzzling. The 1400 cm.$^{-1}$ band, as noted previously, seems consistent with the presence of ionized carboxyl and, as expected, its intensity diminishes as the chain length increases.

Perhaps one of the most interesting aspects of this work is the possibility of correlating specific chemical groups with absorption bands. Such a correlation appears to be possible with the diglycyl group, II.

$$\text{—NH—CH}_2\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—NH—CH}_2\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—} \qquad (2)$$

The evidence in support of this correlation is as follows. An absorption band between 1000 and 1025 cm.$^{-1}$ appears in each peptide having this grouping. In the glycine homopeptides it is consistently one of the strongest bands and appears even in polyglycine and polyglycine methyl ester which have few strong bands other than those caused by NH, CO and CH groups. The 1015 cm.$^{-1}$ band is absent in glycine but appears strongly in diglycine. Although a band in this region may be present in peptides not containing the diglycyl group, such bands are almost invariably weak. Furthermore, in no case where a diglycyl linkage is known to be present have we not found a band in the region 1005 to 1025 cm.$^{-1}$. The utility of this correlation in proteins and peptides from natural sources remains to be investigated.

The most characteristic absorption band found at frequencies lower than 1000 cm.$^{-1}$ in all peptides is that around 700 cm.$^{-1}$. While this frequency lies close to that shown by Sutherland to be a C–H rocking vibration in long chain hydrocarbons,[11] deuteration of polyglycine by exchange with D_2O (Fig. 6) indicates that at least some contribution is due to the N–H grouping. Since it is probably mainly the H of the amide group which is replaced upon treatment of polyglycine with D_2O and there is a definite decrease in the intensity of absorption of the 700 cm.$^{-1}$ in deuterated polyglycine, it is apparent that the N–H group also contributes to absorption around 700 cm.$^{-1}$. It would appear that the absorption band observed in the region of 700 cm.$^{-1}$ is a characteristic one for peptides, polypeptides,[12] and many (if not all) proteins.

Experimental

Apparatus.—Most of the spectral measurements were made on Perkin–Elmer model 12C spectrometers using sodium chloride prisms. The achieved spectral resolution at 1650 cm.$^{-1}$ was 5 to 6 cm.$^{-1}$ and at 850 cm.$^{-1}$ was about 2 cm.$^{-1}$. These values correspond to spectral resolving powers ($\gamma/\Delta\gamma$) of 300 and 425, respectively. For accurate measurements of the glycine peptides in the 3000 cm.$^{-1}$ region a calcium fluoride prism was used. With the calcium fluoride prism the achieved spectral resolution at 2000 cm.$^{-1}$ was 4 cm.$^{-1}$ and at 3000 cm.$^{-1}$ was 10 cm.$^{-1}$.

Technique.—All samples were measured in the solid state. For the most part well-ground mulls in hexachlorobutadiene were used for the region 4000–2000 cm.$^{-1}$ and mineral oil for the region 2000–650 cm.$^{-1}$. Hexachlorobutadiene seems to be a better mulling agent than the perfluorocarbons for the high frequency region since its index of refraction is higher and it is quite transparent in the thicknesses necessary for infrared work. Polyglycine and poly-L-leucine were also measured as continuous films; the former being cast from dichloroacetic acid and the latter from a benzene solution. The glycine peptides were dried at 100° at 1 mm. for two hours and were then ground immediately under hexachlorobutadiene to minimize water absorption. The hydrated samples used for water vapor absorption studies were prepared by exposing thin layers of the powdered compounds to a relative humidity of 81% for periods of at least two weeks. The deuteration of polyglycine was performed by successive treatments of cast films with D_2O at 100° for 18 hours.

Materials.—Glycine and diglycine were recrystallized commercial preparations.

Glycine calcd. for $C_2H_5NO_2$: N, 18.66. Found: N, 18.74. Diglycine calcd. for $C_4H_8N_2O_3$: N, 21.21. Found: N, 21.37. The triglycine, triglycine methyl ester, tetraglycine, pentaglycine, hexaglycine and polyglycine methyl ester were kindly supplied by Dr. E. F. Mellon of the Eastern Regional Research Laboratory. These were the materials prepared by him and described in ref. 9.

The polyglycine was prepared by polymerization of N-carboxyglycine anhydride and supplied by Prof. R. B. Woodward.

(11) N. Sheppard and G. B. B. M. Sutherland, *Nature*, **159**, 739 (1947).

(12) *Cf.* Fig. 3 of reference 2(a).

We are much indebted to Prof. J. S. Fruton of Yale for supplying us with all the leucine containing peptides (except poly-L-leucine). These peptides had been chromatographically purified.

The poly-L-leucine was prepared in our laboratory by Dr. M. S. Muthana by the polymerization of the corresponding N-carboxy anhydride in benzene solution.

Calcd. for $(C_6H_{11}ON)n$: C, 63.7; H, 9.8. Found: C, 64.0; H, 9.8.

It is a pleasure to acknowledge the technical assistance of Misses A. Asadourian, A. O'Rourke and A. Sutton in the spectroscopic work.

BOSTON, MASSACHUSETTS RECEIVED SEPTEMBER 27, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY OF THE UNIVERSITY OF TEXAS]

The Pressure–Volume–Temperature Relations of 3-Methylpentane

BY H. O. DAY WITH W. A. FELSING

The vapor pressures of 3-methylpentane have been determined for the temperature range of 150 to 231.2°. Equations representing these data are presented and a comparison with previously reported data is made. Compressibility data on the liquid in the range from 80 to 275° are presented tabularly. Calculated values of molar heats of vaporization are also given in tabular form.

Introduction

The research program devoted to the determination of the thermodynamic properties of hydrocarbons has been in progress for a number of years. The properties determined have included compressibilities, heat capacities, heats of vaporization and vapor pressure.[1] A particular objective of this program has been the determination of the compressibilities of the isomeric hexanes; thus Kelso and Felsing[2] determined the pressure–volume–temperature relations for *n*-hexane, 2-methylpentane and 2,3-dimethylbutane, whereas Felsing and Watson[3] reported on 2,2-diethylbutane. The purpose of this investigation was the determination of the compressibilities and the vapor pressures of 3-methylpentane, thereby completing the p–v–T data for the five hexanes.

Previous Investigations

The only recorded p–v–T data for 3-methylpentane within the temperature range of the present investigation are those due to Kay.[4] Kay determined the vapor pressures, the critical constants, and the orthobaric densities of all five of the isomeric hexanes.

Method and Apparatus.—The apparatus used in this investigation has been patterned after that described by Beattie[5] and previously discussed by Kelso and Felsing.[2] Bath temperatures were held constant to ±0.005° by means of a platinum resistance thermometer in conjunction with a Mueller bridge and a photoelectric cell relay. The regulating platinum resistance thermometer, calibrated by the National Bureau of Standards, also determined the thermostat temperature. Samples of liquid 3-methylpentane of various sizes were introduced into the glass liner (for the pressure bomb) in the usual manner of distillation under a vacuum; these liners containing the samples were introduced into the pressure bomb as previously described.[2]

Four separate samples of 3-methylpentane were subjected to both vapor pressure and compressibility measurements. The vapor pressures were determined at different relative values of liquid and vapor volume; they were found to be independent of volume over a large range, which behavior is indicative of high purity.

At higher temperatures (200° and above), the imposition of high pressures caused a slight decomposition of the 3-methylpentane. This resulted in an increase in the vapor pressure and, also, the vapor pressure was no longer independent of the volume (increased as the specific volume decreased). If high pressures were avoided, the decomposition was extremely slow and, hence, vapor pressure measurements on a given sample were always completed before the compressibility runs were made.

The Material Used.—The 3-methylpentane was part of a 100-g. sample of research grade 3-methylpentane produced by the Phillips Petroleum Company. The stated purity of the product was given as 99.80 mole per cent., a value determined by an infrared scanning comparison with a National Bureau of Standards product of known purity.

This hexane was distilled into a glass reservoir, discarding the first and last portions. All distillation was done under a vacuum at very low temperatures. It was then distilled under a vacuum into the various calibrated glass liners used in the pressure bomb.

The Experimental Data.—The vapor pressures are presented in Table I, and the compressibilities in Table II.

TABLE I

EXPERIMENTAL VAPOR PRESSURES OF 3-METHYLPENTANE

Temp., °C.	150	175	200	225	231.2[a]
Vapor press., atm.	8.197	12.868	19.286	27.983	30.616

[a] Critical point according to Kay.[4]

Treatment of Data and Discussion.—Two equations were found to express the relationship of vapor pressure to temperature, each covering a definite temperature range:

Range 150–200°: $\log_{10} p(\text{mm.}) = 7.310661 - 1487.9519/T$

Range 200–231.2°: $\log_{10} p(\text{mm.}) = 3.728948 - 636.3719/T + 0.00376627T$

$T = t(°\text{C.}) + 273.16°$. At the higher temperatures, Kay's values[4] differ considerably from the values found in this investigation even after an error[6] in one of Kay's deviation charts has been taken into account; no explanation can be offered at present for the differences.

Kay[4] compared his experimental vapor pressures of *n*-hexane and 2,3-dimethylbutane with those of

(1) (a) W. A. Felsing, A. M. Cuellar and W. M. Newton, THIS JOURNAL, **69**, 1972 (1947); W. A. Felsing and G. M. Watson, *ibid.*, **64**, 1822 (1942), and **65**, 780 (1943); (b) D. H. Templeton and D. D. Davies with W. A. Felsing, *ibid.*, **66**, 2033 (1944); B. P. Dailey with W. A. Felsing, *ibid.*, **65**, 42 (1943); (c) J. F. Lemons with W. A. Felsing, *ibid.*, **65**, 46 (1943); and (d) H. O. Day and D. E. Nicholson with W. A. Felsing, *ibid.*, **70**, 1784 (1948).

(2) E. A. Kelso with W. A. Felsing, *ibid.*, **62**, 3132 (1940), and *Ind. Eng. Chem.*, **34**, 161 (1942).

(3) W. A. Felsing and G. M. Watson, THIS JOURNAL, **65**, 1889 (1943).

(4) W. B. Kay, *ibid.*, **68**, 1336 (1946).

(5) J. A. Beattie, *Proc. Am. Acad. Arts Sci.*, **69**, 389 (1934).

(6) Private communication from Professor W. B. Kay.