more remote branching would not be expected to alter the curve appreciably from that of 2-methyl-2-dodecenoic acid. The absence of a 10.1 μ band in the spectrum of 2,5-dimethyl-2-heptadecenoic acid rules out at least one isomeric form of this structure. The available spectra do not provide any basis for a choice from among the other most likely structures.

NOTE ADDED IN PROOF.—Recently a sample of synthetic 2,4-dimethyl-2-dodecenoic acid has become available from Professor Cason,[5] and its infrared spectrum has been examined. In the region beyond 10 μ, absorption bands are found at the following wave lengths (values for the corresponding bands of C_{27}-phthienoic acid—see Figs. 3 and 4—are given in parentheses for comparison): 10.05 (10.06), 12.3 (12.50), 13.2 (13.26), 14.9 (14.92) μ. Considered together with previous evidence, these data indicate that the second branching methyl group of C_{27}-phthienoic acid is in the γ-position.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, FACULTY OF SCIENCE, TOKYO UNIVERSITY]

Near Infrared Spectra of Compounds with Two Peptide Bonds and the Configuration of a Polypeptide Chain. III

BY SAN-ICHIRO MIZUSHIMA, TAKEHIKO SHIMANOUCHI, MASAMICHI TSUBOI, KENJI KURATANI, TADAO SUGITA, NOBORU MATAGA AND REISUKE SOUDA

RECEIVED SEPTEMBER 8, 1952

The near infrared spectra of acetylglycine N-methylamide, acetylalanine N-methylamide, acetylleucine N-methylamide, acetylglycine ethyl ester and acetylleucine ethyl ester have been measured in the solid state with polarized incident radiation. For the ethyl esters the absorption measurements in carbon tetrachloride solutions have also been made. From the experimental results configurations of the associated molecules have been suggested.

In a previous work we measured the near infrared spectra of carbon tetrachloride solutions of acetylglycine N-methylamide (AGNA), acetylalanine N-methylamide (AANA), acetylleucine N-methylamide (ALNA) and acetylproline N-methylamide (APNA) and found that the molecules of AGNA, AANA and ALNA exist in the extended and folded forms, while those of APNA exist only in the folded form.[1]

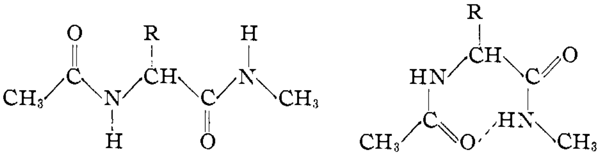
Extended form Folded form

Fig. 1.—The two forms of acetyl aminoacid N-methyl amide.

Our absorption measurements could also show the presence of associated molecules at a concentration as low as 10^{-4} mole/l. for the solutions of AGNA, AANA and ALNA, while there was found no indication of such associated molecules for the solution of APNA even at a concentration as high as 0.05 mole/l.

In order to obtain further information about the structure of the associated molecules of AGNA, AANA and ALNA we have made absorption measurements in the solid state with polarized infrared radiation. In addition, measurements have been made on acetylglycine ethyl ester and acetylleucine ethyl ester in the solid state and in solutions, and the molecular configurations of these ethyl esters have been discussed in relation to those of the N-methylamides.

Acetylleucine N-Methylamide.—As shown in Fig. 2 we observed only two absorption peaks at 3.04 μ and at 3.22 μ in the 3 μ region (from 2.8 to 3.3 μ) and one at 6.19 μ (1616 cm.$^{-1}$) in the 6 μ region for ALNA in the crystalline state. The former two are assigned to the NH stretching vibrations and the latter one to the CO stretching vibration.[2] It is evident from the wave length values of these peaks and from the absence of the 2.9 μ band that the NH and CO groups are involved in hydrogen bonding and are in the *trans* position with respect to each other.[3]

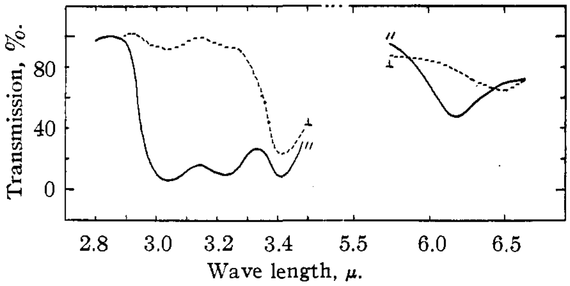

Fig. 2.—Transmission of polarized infrared radiation in the oriented crystal of ALNA.

The solid line of Fig. 2 corresponding to the strong absorption of the NH and CO bands was obtained when the electric vector of the polarized incident radiation was parallel to the long direction of the crystal and the dotted line corresponding to the very weak or almost no absorption was obtained when the electric vector was perpendicular to it. This would mean that the direction of the N—H· · · O hydrogen bond is parallel to the long direction of the crystal and the molecules of ALNA in the lattice are oriented as shown in Fig. 3. Then it would

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(1) S. Mizushima, T. Shimanouchi, M. Tsuboi, T. Sugita, K. Kurosaki, N. Mataga and R. Souda, THIS JOURNAL, **74**, 4639 (1952).

(2) S. Mizushima, T. Shimanouchi, M. Tsuboi, T. Sugita, E. Kato and E. Kondo, *ibid.*, **73**, 1330 (1951).

(3) S. Mizushima, T. Shimanouchi, S. Nagakura, K. Kuratani, M. Tsuboi, H. Baba and O. Fujioka, *ibid.*, **72**, 3490 (1950); M. Tsuboi, *Bull. Chem. Soc. Japan*, **22**, 215, 255 (1949).

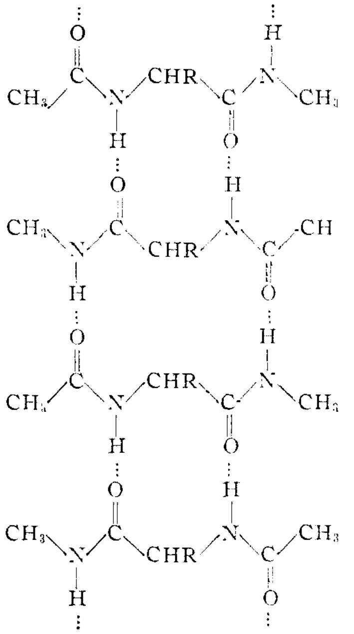


Fig. 3.—Structure of associated molecules of acetylamino acid N-methylamide.

be quite natural to assume that the molecules are associated in a similar manner in carbon tetrachloride solutions[1]: in other words the molecules in the extended form are associated through double hydrogen bonds. This is in agreement with the fact that the association of ALNA is much stronger than that of N-methylacetamide, the molecules of which are associated through single hydrogen bond.[3] It is worthy of note that although the single molecules of ALNA are in both the extended and the folded forms, they take only the extended form in the associated state.

Acetylglycine N-Methylamide and Acetylalanine N-Methylamide.—As shown in Fig. 4 the NH absorption peaks of AGNA and AANA in the solid state have been observed at the same wave lengths as crystalline ALNA. It is probable that the molecules of these two substances are associated in a similar manner as that of ALNA. However, we could not obtain well oriented crystals with which we could show the marked dichroism as in the case of ALNA (the dichroic ratio was found to be (1:25 ∼ 1:3) for these two substances).

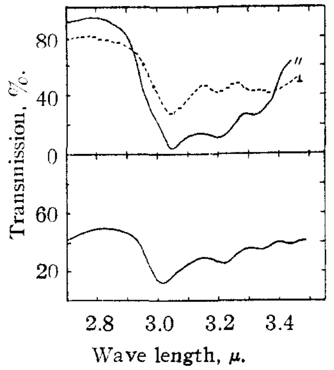


Fig. 4.—Transmission of infrared radiation in the crystals of AGNA (lower) and AANA (upper).

Acetylglycine Ethyl Ester and Acetylleucine Ethyl Ester.—The infrared spectra in the 3 μ region have been observed for acetylglycine ethyl ester (AGEt) and acetylleucine ethyl ester (ALEt) in carbon tetrachloride solutions and in the liquid and crystalline states. The absorption curves are shown in Fig. 5, from which we can conclude that in the liquid and crystalline states the molecules of these two substances are associated almost completely; but in carbon tetrachloride solutions they are associated to an extent much less than those of the three acetyl amino acid N-methylamides referred to above or even those of N-alkylacetamides reported in our previous papers.[1,2,3] In the carbon tetrachloride solution at the concentration of 0.05 mole/l. almost all the molecules of ALNA have been found to be associated.[1] This is also the case even for N-alkylacetamides. However, as shown in Fig. 5 absorption peaks arising from associated molecules of AGEt and ALEt are much less pronounced at the same concentration.

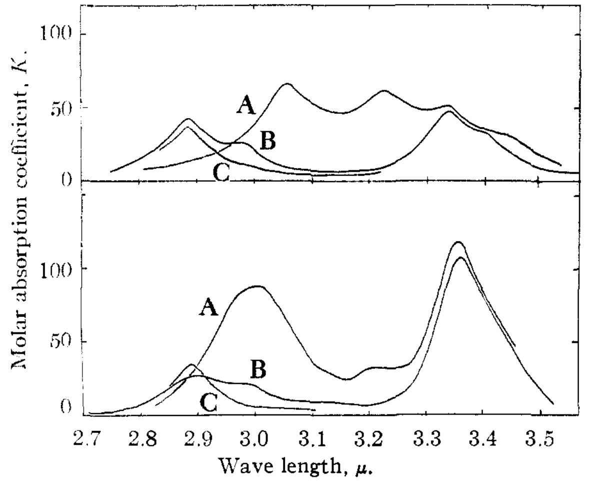


Fig. 5.—Acetylglycine ethyl ester (upper): A, cryst.; B, 500/10000 mole/l. in CCl_4; C, 25/10000 mole/l. in CCl_4, 5/10000 mole/l. in CCl_4. Acetylleucine ethyl ester (lower): A, pure liquid; B, 500/10000 mole/l. in CCl_4; C, 25/10000 mole/l. in CCl_4, 5/10000 mole/l. in CCl_4.

As to the molecular configuration of AGEt in the crystalline state, we could obtain further information by the use of polarized infrared radiation. In the oriented crystal of AGEt the NH bands at 3.05 μ and 3.22 μ and the peptide CO band at 6.06 μ (1650 cm.$^{-1}$) showed marked perpendicular dichroism and the ester CO band at 5.8 μ parallel dichroism as shown in Fig. 6. This experimental re-

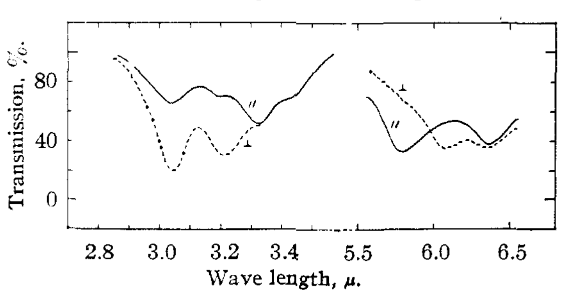
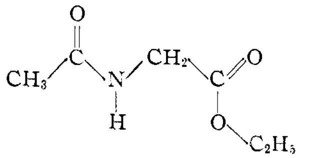


Fig. 6.—Transmission of polarized infrared radiation in the oriented crystal of AGEt.

sult may be considered to indicate in the first place that the NH bond and the peptide CO bond are almost parallel to each other and, accordingly, the peptide bond has a planar *trans* configuration as in the case of N-methylacetamide[3] and acetylamino acid N-methylamides.[2] It may show in the second place that the angle between the peptide CO bond and the ester CO bond is not much different from the right angle and the molecular configuration of AGEt in the crystalline state cannot be the extended form as in the case of ALNA. A probable form would be



A completely folded form just like that shown in Fig. 1 may also be possible. It is easily seen that even the partially folded form shown above would not be as readily associated through intermolecular hydrogen bond as the extended form, while the completely folded form would have the least tendency to be associated. Thus we can see the reason why the association of this substance is less pronounced as compared with N-methylacetamide, for which no hindrance of the intermolecular hydrogen bond can occur.

The experimental results obtained in the present work provide us with further information regarding the structure of some simple molecules which would permit the reliable prediction of the structure of the polypeptide chain.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Photolysis of Some Mercury Dimercaptides

BY R. J. KERN[1]

RECEIVED SEPTEMBER 29, 1952

When mercury dibenzyl mercaptide is photolyzed in benzene solution, mercury, mercuric sulfide, benzyl disulfide, dibenzylbenzal mercaptal and benzyl sulfide are formed. Mercury diphenyl mercaptide forms free mercury but no mercuric sulfide under the same conditions. Six mercury dimercaptides were found to vary markedly in their susceptibilities to photolysis in the solid state the order of increasing stability being benzyl, *n*-propyl, isopropyl, cyclopentyl, *t*-butyl and phenyl.

In the course of preparing derivatives of thiols it was noticed that mercury dimercaptides turned dark on standing, a fact previously recorded by Marcker.[2] A black precipitate insoluble in benzene and a benzene-soluble mixture formed on the photolysis of a benzene solution of mercury dibenzyl mercaptide under nitrogen. Analysis of the insoluble solids indicated 96.3% mercury and 3.5% sulfur which corresponds to 77% of total mercury in the elemental state and 23% as mercuric sulfide. The benzene-soluble portion consisted of 78% benzyl disulfide, 13% dibenzylbenzal mercaptal and a small amount of benzyl sulfide.

A dimercaptide molecule may be considered as decomposing in some manner *via* either (1) or (2). If 77% of the mercaptide molecules decompose

$$(C_6H_5CH_2S)_2Hg \longrightarrow 2[C_6H_5CH_2S\cdot] + Hg^0 \quad (1)$$

$$(C_6H_5CH_2S)_2Hg \longrightarrow [C_6H_5CH_2S\cdot] + [C_6H_5CH_2\cdot] + HgS \quad (2)$$

according to (1) and 23% by (2) then dimerization of the organic units in (1) would theoretically give rise to 79% benzyl disulfide in the organic products.

Mercury diphenyl mercaptide irradiated under the same conditions produced only free mercury and no mercuric sulfide. Lecher[3] found this also to be the case on pyrolysis of this compound. Mercury from the photolysis of mercury dicyclopentyl mercaptide appeared 72% in the elemental state and 28% as mercuric sulfide.

The difference between the photolyses of benzyl and phenyl analogs may be related to the relative stabilities of the corresponding thio-free radicals. The thiophenyl radical would be expected to receive greater stabilization due to resonance structures not available to the thiobenzyl radical. Being relatively more stable only thiophenyl radicals and free mercury are formed from the diphenyl mercaptide while an alternative course of decomposition is also followed by the dibenzyl compound resulting in formation of mercuric sulfide. Phenyl disulfide dissociates to a greater degree than benzyl disulfide as indicated by the fact that when used as photosensitizers in the photopolymerization of styrene 93% conversion is effected by the former compared to 20% by benzyl disulfide under identical conditions.[4]

Six mercury dimercaptides were prepared and irradiated in the solid state by a cold germicidal lamp producing essentially 2537 Å. radiation. These compounds could be arranged in a series according to susceptibility to photolysis judging this by the extent of discolorations under as nearly identical radiation conditions as could be obtained. The benzyl member was the most susceptible turning a jet black color while the phenyl member remained practically unaffected. The series in apparent decreasing susceptibility under these conditions was benzyl > *n*-propyl > isopropyl $\cong$ cyclopentyl > *t*-butyl > phenyl. These differences were not apparent when photolyses were carried out in benzene solution.

(1) Monsanto Chemical Co., Dayton 7, Ohio.

(2) C. Marcker, *Ann.*, **136**, 81 (1865).

(3) H. Lecher, *Ber.*, **48**, 1425 (1915).

(4) L. M. Richards, U. S. Patent 2,460,105 (949).