

225° at 7 mm. and yielded 43 g. or 80%. Upon dissolving in 100 ml. of hot ligroin (70–90°) and standing overnight, crystals were obtained, m. p. 76.5°.

Procedure II. A Grignard solution prepared from 60 g. of 3-bromo-6-methoxytoluene and 8 g. of magnesium turnings in 200 ml. of dry ether was refluxed while 54.4 g. of benzophenone in 100 ml. of dry ether was added. Procedure I was then followed, producing a yield of 45 g. or 50%, m. p. 76.5°.

Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.85; H, 6.62. Found: C, 82.70; H, 6.52.

Preparation of 3-Methyl-4-methoxytriphenylbromomethane.—Ten grams of the crystalline carbinol II was dissolved in 25 ml. of ligroin (70–90°) at the boiling temperature and 4.1 g. of acetyl bromide was added dropwise. Upon gradual evaporation of the solvent at ordinary temperature, a very hard crystalline product separated. Upon decantation of the mother liquor, and washing of the crystals with a small quantity of ligroin, it was placed in a vacuum desiccator. Without further purification, 8 g. or a 66% yield of material, m. p. 106°, was obtained.

Anal. Calcd. for $C_{21}H_{19}OBr$: Br, 21.77. Found: Br, 21.04.

Preparation of 3-Methyl-4-methoxyphenyltriphenylmethane.—Six grams of crystalline product III, was dissolved in 50 ml. of dry ether and treated with 5-ml. portions of a filtered Grignard solution made from 5 g. of bromobenzene. When all the Grignard reagent had been added

the solution became deep red and after one-half hour it was poured into 250 ml. of water containing 10 ml. of concd. hydrochloric acid. The ether layer was separated and the water layer extracted twice with ether. The combined ether extract was washed with 10% sodium carbonate, then dried and evaporated to a gummy residue which could be crystallized from alcohol with a yield of 3.2 g. or 53%, m. p. 162°. No depression in a mixed melting point with the methylated rearranged ether⁶ proved the identity of the substance prepared in these two ways.

Anal. Calcd. for $C_{27}H_{24}O$: C, 88.97; H, 6.64. Found: C, 89.10; H, 6.63.

A derivative V of the synthetic product was produced by treatment of 0.2 g. dissolved in glacial acetic acid with an equivalent of bromine. This derivative, when recrystallized from alcohol, agreed in properties and m. p. of 185° with the same material prepared by two different methods.^{4,6}

Summary

3-Methyl-4-methoxyphenyltriphenylmethane has been synthesized and found to correspond to the methyl ether of Schorigin's rearranged product. Consequently, in the rearrangement of the triphenylmethyl ether of *o*-cresol, the triphenylmethyl radical has migrated to the para position of the *o*-cresol nucleus.

DURHAM, NEW HAMPSHIRE RECEIVED AUGUST 2, 1940

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Infrared Absorption Studies. XI. NH-N and NH-O Bonds

BY A. M. BUSWELL, J. R. DOWNING AND W. H. RODEBUSH

The observation of the shift to longer wave length of the fundamental infrared absorption band of hydroxyl in certain molecules was suggested in earlier papers¹ as a simple spectroscopic test for hydrogen bonds. This test has been verified by so many examples in the case of hydroxyl compounds that certain authors have been inclined to attribute every change in frequency to hydrogen bond formation.² This tendency is likely to lead to confusion and erroneous conclusions since frequency shifts may be due to other causes than hydrogen bond formation. In a recent publication³ the authors have pointed out some of the factors which must be given consideration when the methods of infrared spectroscopy are used as a test for nitrogen hydrogen bonds.

The only rule of general applicability to the frequency shift in hydrogen bond formation is

(1) Buswell, Deitz and Rodebush, *J. Chem. Phys.*, **5**, 84 (1937); Errera and Mollett, *Chem. Rev.*, **20**, 59 (1937).

(2) Gordy and Stanford, *THIS JOURNAL*, **62**, 501 (1940).

(3) Buswell, Downing and Rodebush, *ibid.*, **61**, 3252 (1939).

that of Venkateswaran⁴ who states that the shift will be greater the more acidic the hydrogen. In the case of chloroform-acetone complexes the hydrogen is very slightly acidic and the shift in frequency is so small that it would not have been observed had the existence of the complex not been indicated by other data.⁵ The increase in molar absorption coefficient is in this case a much more certain test for hydrogen bond formation than the shift in frequency.

But the molar absorption coefficient may also vary for other reasons than bond formations. In the case of aniline which was not fully discussed in our previous paper¹ we find in dilute carbon tetrachloride a doublet due to the NH_2 group with peaks at 2.87 and 2.93 μ . In pure liquid aniline we find a fairly narrow, single (unresolved) peak at 2.97 μ . This shift could be due to change in dielectric constant rather than hydrogen bond-

(4) Venkateswaran, *Proc. Indian Acad. Sci.*, **7**, 13 (1938).

(5) Buswell, Rodebush and Roy, *THIS JOURNAL*, **60**, 2528 (1938).

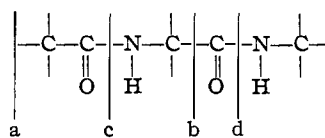
ing. Carbon tetrachloride has a dielectric constant a little greater than 2 while liquid aniline has a dielectric constant greater than 7.0. The theory of Kirkwood while not exact shows that a shift to lower frequency with higher dielectric constant is to be expected. West and Edwards⁶ have shown that the fundamental frequency of hydrogen chloride is shifted by 50 cm.^{-1} in passing from the dilute carbon tetrachloride solutions to pure liquid hydrogen chloride. The shift of some 85 cm.^{-1} in the case of aniline is of the same order of magnitude and the theory is not sufficiently precise to say whether the shift should be greater or less than that for hydrogen chloride. Hence we must appeal to other evidence for the confirmation of bond formation in aniline. In the case of pure liquid aniline this becomes a search for evidences of association.

Apparently the only general criterion for all types of associations ranging from that found for the carboxylic acids to that existing in water or hydrogen fluoride is the Trouton constant. Any type of association known, appears to cause a deviation of this constant from its normal value of about 21 for liquids boiling above 100° . Freezing points and boiling points are unreliable criteria of association, because association may be present in all three phases in varying degrees. Dielectric constant is likewise an uncertain criterion unless it is abnormally high.

Since the Trouton constant for aniline is normal and the dielectric constant about what one would expect for an unassociated polar molecule it follows that the association must be very small indeed. Since aniline does not behave like the alcohols which form glasses and have a high dielectric constant we may suspect that the complexes present are limited to dimers. In view of the foregoing consideration one may well question if the spectroscopic data indicate bonding at all. The increase in molar absorption coefficient is accounted for by the increase in dipole moment with increasing dielectric constant of the environment, that is predicted by Onsager.⁷ The whole point in the case of aniline is the small tendency toward the formation of NH-N bonds between two molecules, in other words the small energy associated with such bonds. It so happens that energy of the hydrogen bond in a number of examples, *e. g.*, chloroform-acetone, amounts to some 5000-6000

calories. The authors do not wish to set up a minimum energy as an arbitrary criterion for hydrogen bond formation but they do wish to point out that when the bonding energy is only a few hundred calories it is difficult to distinguish between the various types of possible interaction such as van der Waals forces, etc. And it becomes difficult to make positive statements that hydrogen bonding is present. Small shifts in absorption frequencies do not inevitably point to hydrogen bonding.

Hydrogen Bonding and the Protein Problem.—Protein molecules involve the peptide linkage repeated in chains.



An infrared absorption spectrum is obtained in the 3μ region which is characteristic of all proteins.⁸ This spectrum indicates hydrogen bonding and it is the commonly accepted belief that hydrogen bonding occurs between adjacent chains. It becomes desirable, therefore, to determine the exact location of these bonds, that is, whether they are NH-N or NH-O bonds in order to determine the structure of proteins. Furthermore if we include any essential portions of this chain in a molecule such as a dipeptide⁹ or N-substituted amide we obtain the same spectrum (Fig. 1) and in these cases the variation with concentration shows that the bonding is intermolecular as has been supposed in the case of the proteins. Finally, in the case of a molecule such as carbethoxypyrrole, we find a similar spectrum, reproduced herewith (Fig. 2), and we see that carbethoxypyrrole does include the essential functional groups of the peptide linkage. The chain has been cut, *c. d.*, instead of *a, b* as for the amides. The essential feature of the spectrum in the foregoing cases is a very strong peak in the neighborhood of 3.00μ and a (usually) weaker absorption at 3.22μ . Both peaks disappear on dilution in the case of the simple molecules mentioned above so that they are indicative of hydrogen bonding. In the case of carbethoxypyrrole it is not certain that the 3.22μ peak is present at all. Our problem is to determine the exact type of hydrogen bonding that causes the absorption. We shall

(6) West and Edwards, *J. Chem. Phys.*, **5**, 14 (1937).

(7) Onsager, *THIS JOURNAL*, **58**, 1486 (1936).

(8) Work by Dr. K. F. Krebs in this Laboratory to appear shortly.

(9) Buswell, Rodebush and Roy, *THIS JOURNAL*, **60**, 2444 (1938).

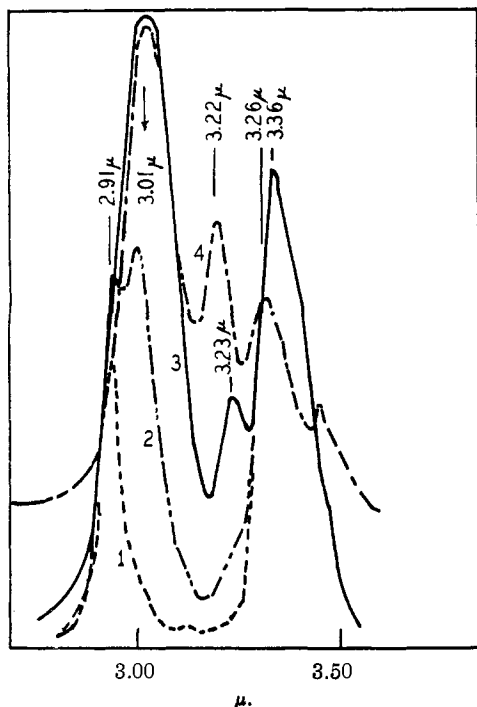


Fig. 1.—Acetylglycine ethyl ester: (1) 0.004 *M*; (2) 0.064 *M*; (3) 0.256 *M*; (4) solid.

assume at the outset that the bonds are either NH-N or NH-O. The possibility of a reciprocal enolization to produce an OH-N cannot perhaps

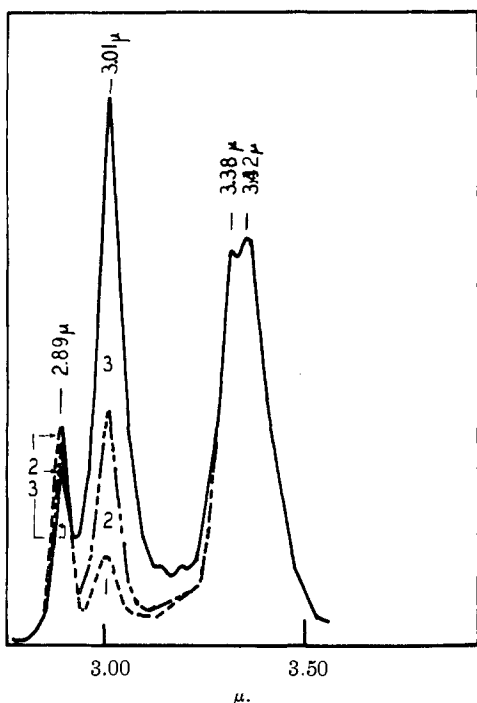


Fig. 2.—3,5-Dimethyl-2-carboxypyrrrole: (1) 0.002 *M*; (2) 0.008 *M*; (3) 0.128 *M*.

be eliminated but there is evidence that it does not take place to any great extent.¹⁰

The direct attack to this problem involves the formation of NH-N and NH-O bonds between unlike molecules so that the "natural" frequency if such exists for such a type of bond can be observed. This we have attempted to do. It is clearly indicated that the failure of nitrogen compounds to form bonds is due to the weakly acid character of the hydrogen attached to nitrogen. In the case of the amides when the acid character is more pronounced the association through hydrogen bonding is very strong indeed. Accordingly a less basic amine, *viz.*, diphenylamine was studied. Diphenylamine has an N-H absorption at 2.89 μ almost exactly the same as N-substituted acetamide and with a basic nitrogen such as pyridine, Fig. 3, it shows a strong absorption at 3.03 μ . Here there can be no question that the

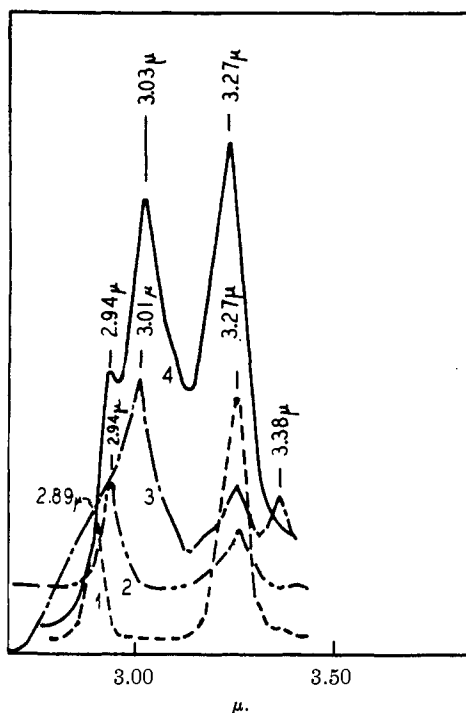


Fig. 3.—(1) Diphenylamine in carbon tetrachloride solution: 0.004 *M*; (2) solid diphenylamine; (3) diphenylamine (1 g.) and dimethylacetamide 1 cc.; (4) diphenylamine (1.7 g.) and dimethylacetamide 1 cc.

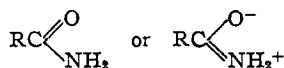
NH-N bond is present. With dimethylacetamide the absorption is at 3.03 μ . One might take this as a confirmation that a strong absorption in the 3 μ region is always due to NH-N bonding.

(10) Mr. McMillan in this Laboratory has shown that the characteristic absorption of the carbonyl group is present in all cases, although it may be considerably modified.

There are several questions to be explained, however. Pyrrole in which the H-N frequency is not greatly different from diphenylamine gives an absorption at 3.11μ , when an NH-N bond is formed with pyridine. Furthermore neither pyrrole nor diphenylamine shows any appreciable tendency to associate whereas the amides are very strongly associated. One must recognize that this difference in behavior may be very significant. Finally we have been unable to obtain any evidence at all for NH-O bonds between unlike molecules. Diphenylamine shows no evidence of bonding with a variety of molecules containing carbonyl or ether oxygen. All of these facts must be taken in account in any conclusions that may be drawn.

The absence of association in the aromatic amines is undoubtedly due to resonance. One of the important structures in the resonance theory is the quinoid form in which the nitrogen forms a double bond with the carbon of the ring and thereby becomes positive. A nitrogen atom in this condition may readily furnish an acidic hydrogen but cannot act as an electron donor since it has no electrons to donate. If there is a possibility of enolization as in the case of *o*-nitroacetanilide, the enolic form is likely to prevail. The frequency observed for *o*-nitroacetanilide 2.96μ would agree with the assumption of a chelated enolic form. On the other hand 6-methyl-2-nitroacetanilide is not chelated because of the interference between the methyl group and the groups on the nitrogen. Work in this Laboratory¹¹ shows that methyl groups in similar situations interfere with coplanarity and the nitrogen becomes basic as in the aliphatic amines. A familiar striking example is methylacetanilide, which is a much stronger base than acetanilide.

Pyrrole has a similar possibility of resonance with the formation of a positive nitrogen atom so that its behavior is similar to that of diphenylamine. It then remains to show why the amides with somewhat similar resonance configurations should associate so strongly. Pauling¹² has shown that because of resonance the atomic configuration of the amides must be



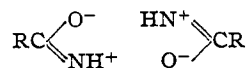
(11) M. T. O'Shaughnessy, Jr., and W. H. Rodebush to be published shortly.

(12) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 125.

The resonance contribution to the energy is estimated as 21 kilocalories which means that the second form must be one of the important structures in the resonance. If Pauling's conclusions are correct they constitute an overwhelming argument for the existence of NH-O bonds in the association of amides. With the second structure the NH-O bond is the only one possible: an NH-N is possible in the first structure but it would not be very strong and it would certainly freeze the structure and destroy the resonance, thus losing 21 kilocalories of energy. This, of course, will not happen. Acetanilide itself behaves as do the amides showing strong association while aniline and diphenylamine do not. The explanations must, therefore, lie in the possibility of the second structure and the NH-O bond.

It remains to consider what objections may be raised to the foregoing conclusions. It must be emphasized that the oxygen in this type of bond is the negative oxygen attached to carbon by a semi-polar bond. The failure of diphenylamine to form an NH-O bond with carbonyl oxygen is, therefore, not surprising since this oxygen is less polar than the oxygen of the amide group. Furthermore, according to our infrared evidence diphenylamine forms a bond with dimethylacetamide and diphenylacetamide but not with diphenylbenzamide. Also benzanilide shows no tendency toward association. The presence of the benzoyl group in an amide should favor the structure $\text{C}_6\text{H}_5\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{NHR} \end{array}$ as against the structure $\text{C}_6\text{H}_5\text{C} \begin{array}{l} \diagup \text{O}^- \\ \diagdown \text{NHR}^+ \end{array}$. At the least one may say that since the first structure is the only one that permits bonding to the nitrogen the absence of bond formation indicates that bonding is to the semi-polar oxygen rather than to the nitrogen.

Once we grant the above conclusions, it becomes necessary to consider the possibility of dimer formation that is suggested by the analogy between the amides and the carboxylic acids. This possibility has been discussed by some of us in a previous article.¹³



The postulate of intermolecular enolization made at that time must be ruled out for the same reason that we ruled out intramolecular enolization

(13) Buswell, Rodebush and Roy, THIS JOURNAL, 60, 2239 (1938).

above. The analogy with the carboxylic acids is, therefore, incomplete. In the symmetrical ring of the carboxylic acids we observe four frequencies. In the amide ring we should observe only one because of the lack of symmetry in the chemical group. This frequency should involve the antisymmetric vibration of the two bonded hydrogens and should be lower in frequency than a single bonded hydrogen.

The foregoing predictions appear to be verified by our infrared observations. In carbethoxyppyrrole the carbonyl and nitrogen are separated by an additional carbon atom. This separation probably either prevents the formation of ring dimers or if they are formed, prevents the interaction between the two hydrogens so that only a single frequency 3.01μ is observed and certainly this may be taken as the normal frequency of the single NH-O⁻ bond. Hence, we conclude that with an amide such as N-ethylacetamide which shows primarily a 3.00μ absorption but with increasing concentration one at 3.22μ , the first frequency represents a single linkage between two molecules and the second frequency is due to the closure of the ring by a second NH-O⁻ bond.

In the preceding discussion we have considered only molecules which resemble the peptide group in that there is only one hydrogen attached to the nitrogen. If we consider acetamide which contains the NH₂ frequency we find that the main association peak is at 3.13μ and that a peak in the neighborhood of 3.00μ appears only at higher concentrations. We conclude that the 3.13μ absorption is due to the ring dimer as was the 3.22μ absorption in the N-substituted amides, only now the ring dimer is formed much more readily since it appears first at lower concentrations. This is easily explained since resonance requires a coplanar configuration and hence *cis* and *trans* forms for the amide group. In order to form a ring in the N-substituted amides the forms in which the hydrogen is *cis* to the oxygen must come together. The probability of this happening is, therefore, one-fourth, assuming an equal distribution of *cis* and *trans* forms. Acetamide itself cannot fail to form a ring and undoubtedly does so at low concentrations. The 3.01μ frequency that appears at higher concentrations and persists in the solid crystal must be due to the second hydrogen on the nitrogen which is *trans* to the oxygen, bonded to the oxygen of another molecule. The conclusions drawn above receive a good deal of confirmation

from the infrared absorption of certain related molecules whose crystal structure has been determined by X-ray diffraction. While one must be careful in comparing infrared absorption in the crystalline state with that of the solution it appears that the amides and similar molecules do not show any marked difference in the two states as may be seen by reference to Fig. 4 which shows the absorption of solid films.¹⁴ Diketopiperazine

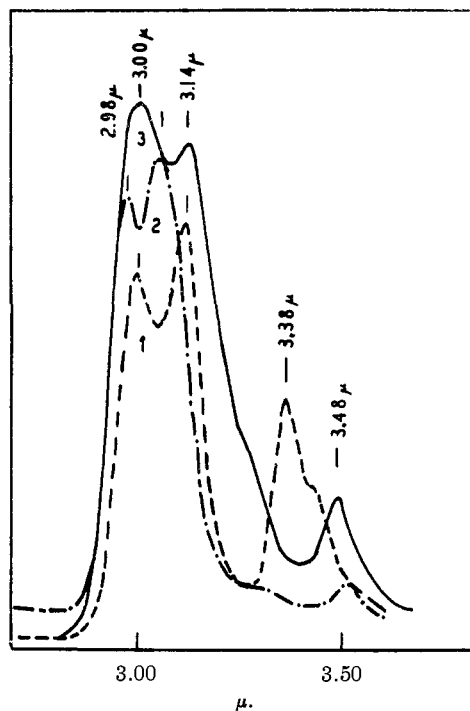


Fig. 4.—Solid films: (1) acetamide; (2) trichloroacetamide; (3) *n*-valeramide.

zine shows a strong absorption at 3.26μ , Fig. 5. This is sufficiently close to the value of 3.22μ which we assumed to be due to ring dimers in the amides. Corey¹⁵ has shown that the crystal structure of diketopiperazine involves just such rings with NH-O⁻ bonds. Diketopiperazine also shows a slight absorption at 3.14μ but this is suspected to be due to glycine, which may be produced as a dissociation product in the preparation of the film.

The absorption spectra of glycine and alanine in thin solid films show very interesting and suggestive relations to the spectra of the amides but

(14) Water and phenol show a marked difference between the wave length of the absorption maximum in the crystal and liquid states. The shift is in the opposite direction to that which might be predicted from the change in the dielectric constant unless it should happen that the second derivative of the dipole moment with respect to the displacement is negative.

(15) Corey, *THIS JOURNAL*, **60**, 1598 (1938).

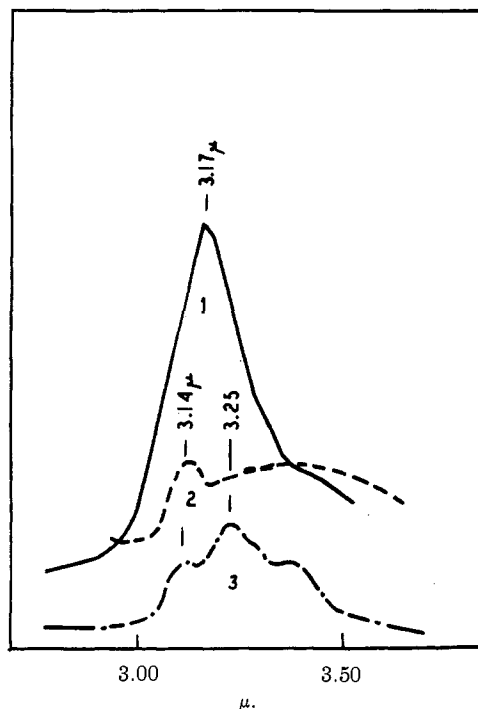


Fig. 5.—Solid films: (1) sulfamic acid; (2) glycine; (3) diketopiperazine.

the interpretation here is by no means simple. Glycine shows an absorption at 3.14–3.16 μ which suggests at once its resemblance to acetamide since both contain NH_2 groups. However, glycine shows no 3.0 μ absorption and its properties, such as high melting point, indicate a zwitterion structure. Albrecht and Corey¹⁶ who studied the crystal structure by the X-ray diffraction methods consider both possibilities but prefer the zwitterion structure. According to them hydrogens on the nitrogen are bonded to oxygens but two of these bonds which lie in a plane are much shorter and stronger than the third NH-O^- bond. The N–O distance is so great in the case of the third bond that it can scarcely be considered a bond at all. It seems a remarkable coincidence that glycine shows a sharp absorption maximum about 3.15 μ as does acetamide. The similarity in the spectrum ends here but one is inclined to suspect that the NH_2 group is involved here as a unit although the ring structure cannot be the same since the glycine molecule contains two oxygens. The coincidence becomes even more striking when one observes that alanine (methylglycine) shows an absorption at 3.23 μ almost exactly the same as the N-substituted amides. While the crystal

(16) Albrecht and Corey, *THIS JOURNAL*, **61**, 1087 (1939).

structure of alanine has not been determined one may imagine that it has a ring structure very similar to the N-substituted amides.

The relation of the foregoing conclusions to hydrogen bonding between protein chains is obvious. Since the absorption spectra for the proteins resemble qualitatively that of the N-substituted amides we must suppose that they contain both isolated NH-O^- bonds and NH-O^- bonds occurring in pairs so that there is interaction between the hydrogen vibrations as in the ring dimers. There are presumably no NH-N bonds at all. We have thus reached the conclusion¹⁷ that an NH-O^- bond will have the same frequency as an NH-N bond. This conclusion seems to be in agreement with the rule of Venkateswaran. Since the hydrogen attached to nitrogen is very slightly acidic and undergoes a small frequency shift (*ca.* 0.1 μ) when the bond is formed, it will make little difference to which atom the hydrogen is bonded. Any further shift in frequency must be due to interaction between the vibrations of two or more hydrogens.

The frequency at 3.15 μ seems to be identified with the NH_2 group and to persist in glycine when the group presumably becomes NH_3^+ . It is interesting to note that sulfamic acid which is presumably SO_3NH_2^+ shows absorption at 3.17 μ , Fig. 5.

It should be noted that the coplanar configuration of the amide group $\text{-C}\begin{matrix} \text{O}^- \\ // \\ \text{N} \end{matrix}$ must persist in the peptide chain of the proteins, thus introducing an additional variable in protein structure, that of *cis*- and *trans*-hydrogen atoms. Denaturation of proteins undoubtedly involves breaking and reforming hydrogen bonds and in this process many hydrogen atoms must be shifted from *cis* to *trans* and *vice versa*.

A more detailed discussion of the application of these ideas to the proteins will be given elsewhere.

Summary

Intermolecular NH-N bonds show a fundamental infrared absorption near 3 μ . These bonds are formed only when the first nitrogen is relatively much more acidic than the second nitrogen.

NH-O bonds are formed only with a semipolar oxygen. The bonding observed by infrared

(17) Dr. M. L. Huggins informs us that the NH-O^- bonds appear much more probable from the structural point of view in the models of protein molecules that are here constructed.

studies in amides and the peptide linkage is believed to be NH-O^- with absorption near 3.0μ if isolated but at 3.22μ if the bonds are formed in pairs. A coplanar structure is postulated for the

CONHR group which involves geometrical isomerism. This structure must be considered in any explanation of protein behavior.

URBANA, ILLINOIS

RECEIVED JULY 12, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Dissociation of Hexaphenyldiplumbane

BY RALPH PRECKEL AND P. W. SELWOOD

Molecular weight determinations by Krause and Reissaus,¹ and, more recently, by Foster, Dix and Gruntfest,² indicate that hexaphenyldiplumbane, $(\text{C}_6\text{H}_5)_3\text{Pb-Pb}(\text{C}_6\text{H}_5)_3$, is appreciably dissociated in dilute benzene solution. The assumption is that the dissociation product is triphenyllead. As triphenyllead possesses an odd number of electrons, magnetic susceptibility measurements should serve to determine the degree of dissociation with some accuracy, and possibly to determine the heat of dissociation.

Two samples of hexaphenyldiplumbane were obtained. One was prepared for this investigation by Dr. J. D. Malkemus of this University, and the other was obtained through the courtesy of Professor Laurence S. Foster of Brown University.

Experimental Part

Magnetic Measurements.—The magnetic susceptibilities were measured by means of the Gouy balance previously described.³ The only modifications were in the use of the differential method of Freed and Kasper⁴ for the investigation of dilute solutions. All measurements on solutions were carried out in the absence of air and of moisture. The amount of light reaching the samples was also restricted, and as a final precaution against decomposition, all measurements were completed within twenty-four hours of the preparation of a solution. The absence of light was necessary because a benzene solution of the diplumbane was found to decompose quickly on exposure to direct sunlight. One of the decomposition products was metallic lead which was deposited as a black mirror.

All measurements were referred to freshly distilled benzene,³ the specific susceptibility of which was assumed to be -0.7023×10^{-6} at 25° . This value is, in turn, referred to water as -0.7200×10^{-6} at 20° .

The field strength for all measurements was 13,100 oersted.

Density Measurements.—Densities of the solutions, necessary for the magnetic susceptibilities, were deter-

mined over the temperature range 30 to 80° by means of an expansion pycnometer. The pycnometer was calibrated by reference to benzene, the density of which, at various temperatures was taken, partly by extrapolation, from the data of Smyth and Stoops.⁵

Preparation of Materials.—One of the samples (Malkemus) of the hexaphenyldiplumbane was prepared by the action of phenylmagnesium bromide on lead dichloride. The other sample (Foster) was prepared by reduction of triphenyllead iodide in liquid ammonia. As shown below, these samples in the solid state had magnetic susceptibilities differing by less than 1%. No further purification was therefore believed necessary.

Two solutions of the diplumbane in redistilled, thiophene-free benzene were used. These were prepared by shaking the benzene with the diplumbane in a completely evacuated set of bulbs which could in turn be attached to the magnetic and density tubes as desired. All transfers of solution were carried out in the complete absence of air.

Analyses of the solutions were made by evaporating to dryness at 125° and weighing the residue.

Results

The susceptibility of the powdered hexaphenyldiplumbane at several temperatures is given in Table I. The susceptibility was independent of

TABLE I

Sample	Temp., °C.	Susceptibility per g. $\times 10^6$
(Malkemus)	25	-0.408 ± 0.002
(Malkemus)	-40	-.408
(Malkemus)	-100	-.396
(Foster)	25	-.404

field strength, proving the absence of ferromagnetic impurities. These data establish the purity of the samples and set an upper limit of dissociation at 0.1%. The slight temperature dependence is probably due to paramagnetic impurities present in extremely small amount. The molar susceptibility of the diplumbane is -356×10^{-6} , as compared with -285×10^{-6} for hexaphenyldigermane.

In order to obtain the susceptibilities of the solu-

(1) Krause and Reissaus, *Ber.*, **55**, 894 (1922).

(2) Foster, Dix and Gruntfest, *THIS JOURNAL*, **61**, 1685 (1939).

(3) Selwood, *THIS JOURNAL*, **61**, 3168 (1939).

(4) Freed and Kasper, *Phys. Rev.*, **36**, 1002 (1930).

(5) Smyth and Stoops, *THIS JOURNAL*, **51**, 3320 (1929).