

# Studies in the Stereochemistry of Quinquevalent Nitrogen. VI.

Configuration of Quinquevalent Nitrogen Compounds.\*

By

**Shigeru Komatsu.**

(Received Feb. 22, 1918.)

---

As it is concerned in structural chemistry, the chemical and physical properties of compounds can be explained by the ways of linking of atoms, and also by their numbers in molecule. There are, however, the substances having the same number of atoms and the same ways of linking in molecule, yet exhibiting the different properties. Such phenomena of isomerism can easily be explained in stereochemistry, taking into consideration the spatial arrangements or relative positions of the atoms or atomic groups in molecule.

Le Bel<sup>1</sup> and van't Hoff<sup>2</sup> proposed to explain the existence of optically active carbon compounds based upon the assumption of the asymmetric carbon atom, and Werner<sup>3</sup> is of the opinion that the atoms or atomic groups in the metal complexes are arranged in space around a metallic atom as centre; in other words the special feature of stereochemistry is not to consider the atoms of equal value in molecule, while it is believed to be the case in structural chemistry.

In stereochemistry, therefore, the chemical and physical properties of compounds should depend principally upon the nature of the central atom. Hence, for the investigation of stereochemistry of nitrogen, the most important factor is to ascertain the nature and directions of its valences.

---

\* A brief preliminary report was published in the Journal of Tokyo Chemical Society, **36**, 445 (1915).

1 Bull. soc. chi., **22**, 337 (1874).

2 Die Lagerung d. Atome im Raume, 1908, p. 4.

3 Lehrbuch d. Stereochemie, 1904, p. 317; Lieb. Ann. 386, 1 (1912); Ueber d. Konst. u. Conf. Verb. höhre. Ord., 1914.

Proteines, vegetable alkaloids and other natural products containing nitrogen in their molecules have not been submitted to chemists as the materials for the stereochemical investigations of the nitrogen atom. Although stereochemistry of carbon compounds was started from the study of the natural product such as betaines, choline &c., the quinquivalent nitrogen compounds found in nature have been considered to be unserviceable for the study of stereochemistry of the quinquivalent nitrogen.

Stereochemistry of the quinquivalent nitrogen drew much attention of many chemists<sup>1</sup> at an early date, but our knowledge of it has not yet advanced beyond what is in fact a mere beginning of study. The reason may be that we could not find out the natural substances favourable for study, and also have met the difficulty for the preparation of the stable compounds.

Considering of the periodic system of elements, the author has been led to conceive that the configuration of the quinquivalent nitrogen compounds can be explained on referring the knowledge of the stereochemistry of carbon compounds and metal complexes so far gained.

The first step of study would be to determine whether the five valences of nitrogen in the ammonium compounds are of equal value or not, and the next the investigation of the spatial configuration of the atoms or atomic groups combined with the nitrogen atom. For the solution of the first problem, the existence or non-existence of optically inactive ammonium compounds must be settled. The question on such a subject has been studied by the author by examining the formation and decomposition of the quarternary ammonium compounds and also their other chemical and physical properties.

In the quarternary ammonium compounds, at least one radical combined with nitrogen is of a negative character, having an electrical nature different from the other four. The quarternary ammonium compounds should be represented by the general formula,  $NR_4X$ ,  $X$  representing the negative atom or atomic group, and their derivatives by the following three types,  $NR_3R'X$ ,  $NR_2R'R''X$  and  $NRR'R''R'''X$ . These compounds are formed by the direct addition of the tertiary.

---

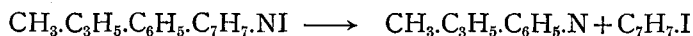
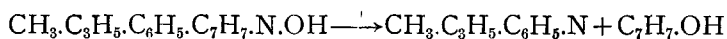
<sup>1</sup> H. Jones, *Stereochemistry of Nitrogen*, 1904; E. Wedekind u. E. Fröhlich, *Z. Stereochemie d. funfw. Stickstoff*, 1907; E. Wedekind, *Die Ent. d. Stereochem. d. funfw. Stick. in letzten Jahrzehnt.*, 1909.

amines and alkyl derivatives RX (BrCN, O<sub>2</sub>, Br<sub>2</sub>, CH<sub>3</sub>CN, C<sub>2</sub>H<sub>5</sub>I, ICH<sub>2</sub>CO<sub>2</sub>.C<sub>2</sub>H<sub>5</sub>&c.) and therefore, there would be several different ways of the formation of the ammonium compounds.

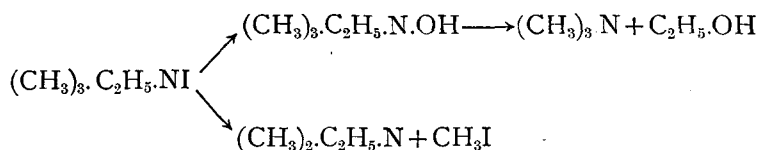
All of the ammonium compounds prepared by different ways were found to be identical by the examination of their melting point, crystalline forms and other physical properties.<sup>1</sup> This seems to stand in favour with the view accepted by a number of chemists about the non-existence of isomer in the inactive ammonium compounds.

With regard to the decomposition<sup>2</sup> of the quaternary ammonium compounds by heat or by electrical means, it may be summarized in the following four types :

1. The ammonium hydroxides and their haloides give the same tertiary amines as seen in methyl allyl phenyl benzyl ammonium compounds :



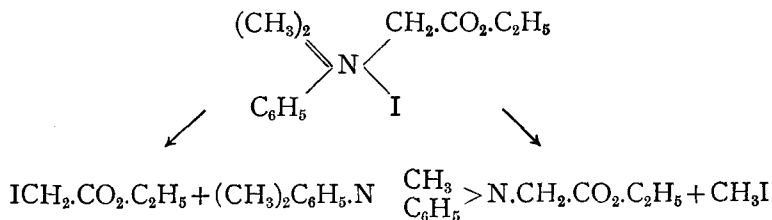
2. The ammonium hydroxides and their haloides give different tertiary amines ; for example, trimethyl ethyl ammonium hydroxide is decomposed into trimethyl amine and ethyl alcohol but its iodide into dimethyl ethyl amine and methyl iodide ;



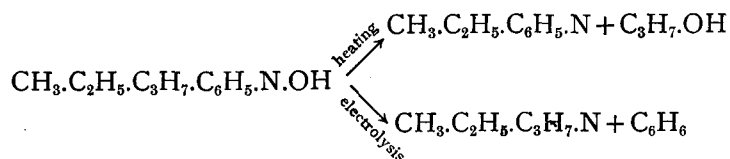
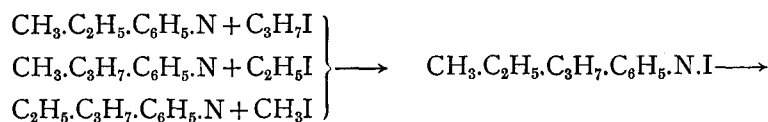
3. As we have seen in the case of dimethyl phenyl ethyl acetate ammonium iodide, the double dissociation of molecule takes place as the following scheme shows :

1 Wedekind, Die Ent. d. Stereochem. d. funfw. Stick. in letzten Jahrzehnt., 1909; Wedekind u. Fröhlich, Z. Stereochem. d. funfw. Stick., 1907, p. 68; Wedekind, Ber. D. chem. Ges., **34**, 3991 (1901); **35**, 183, 3580 (1902); **36**, 1158, 3791 (1903); **37**, 2712, 3894 (1904); Jones, J. Chem. Soc., **85**, 224 (1904); Kipping, Ibid., **83**, 874, 889, 902, 1147 (1903); **87**, 628 (1905); Collie and Schryver, Chem. News, **63**, 174 (1891); Komatsu, Mem. Coll. Sci. Engin., Kyoto, **3**, 371 (1912).

2 Braun, Lieb. Ann. **382**, 1 (1911); **386**, 273 (1912); Singh, J. Chem., Soc., **109**, 780 (1916); Komatsu, Mem. Coll. Sci. Engin., Kyoto, **3**, 371 (1912); Mem. Coll. Sci., Kyoto, **1**, 370 (1916); Wedekind, Ber. D. chem. Ges., **35**, 766, 1075 (1902); Dunlop, J. Chem. Soc., **101**, 1999 (1912); Emde, Arch. Pharm., **249**, 106, 111, 118 (1911); **247**, 369 (1909); Ber. D. chem. Ges., **42**, 2590 (1909); Sidgwick, Organic Chemistry of nitrogen. 1919. p.23.



4. By heating or by electrolysis, methyl ethyl propyl phenyl ammonium hydroxide is decomposed into methyl ethyl aniline or methyl ethyl propyl amine respectively :



Decomposition of the quaternary ammonium compounds being so complex that we can not give a general rule, but throughout all the cases the author has noticed that one and the same ammonium compound prepared from different sources yields the identical tertiary amine by the same treatment. Now it is highly probable that nature of decomposition of the compounds depends upon the mutual influence of the electrical character of the alkyl groups linked to nitrogen, but not upon their relative positions in the molecule, like the double decomposition and substitution in the metal complexes.<sup>1</sup> Such a fact naturally leads us to the hypothesis that the four negative valences of the quinquevalent nitrogen are of the same value. Through the investigations of Meisenheimer and his co-workers<sup>2</sup> and of the author<sup>3</sup> on the derivatives of the types  $(\text{R}_3)\text{N} < \begin{array}{c} \text{OR} \\ \text{OH} \end{array}$  and  $(\text{R})_3\text{N} < \begin{array}{c} \text{OH} \\ \text{OR} \end{array}$  from trialkyl amine oxide  $(\text{R})_3\text{N}:\text{O}$ , there may be drawn a conclusion that the nature of the fifth valence of the nitrogen atom is entirely different from that of four negative valences. For the confirmation of the

<sup>1</sup> Werner, Lieb. Ann., **386**, 1 (1912).

<sup>2</sup> Ibid., **385**, 13, 117 (1912); **397**, 273 (1913); Ber. D. chem. Ges., **41**, 3966 (1909)

<sup>3</sup> Mem. Coll. Sci., Kyoto, **1**, 316 (1916).

above view, the author<sup>1</sup> has also studied the absorption spectra of the quarternary ammonium compounds. The absorption spectra of the ultra violet rays of the quarternary ammonium compounds are independent of the nature of the atom or atomic group (excepting the atomic group which itself has the absorption spectra) combined by the negative valence to the nitrogen, but depends upon that of the atoms or atomic groups combined by the negative valences of nitrogen.

Now, we have to discuss the second problem, i.e., the direction of the valences of the quinquevalent nitrogen or the spatial configuration of the quarternary ammonium compounds. Thus, the different views brought forward by the different investigators, will be stated below :

Fig. I.

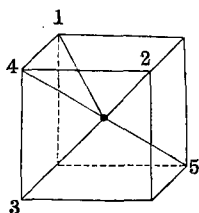


Fig. II.

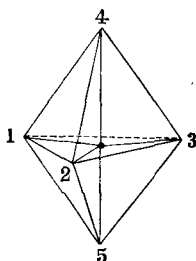
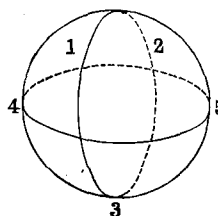


Fig. III.



1. Van't Hoff<sup>2</sup> suggested the cubic configuration, supposing the nitrogen atom to be situated at the centre of a cube, and the five atoms or atomic groups at the five solid angles as shown in Fig. I.

2. Willgerodt<sup>3</sup> proposed the double tetrahedron configuration, modifying van't Hoff's view, as shown in Fig. II.

3. Fröhlich,<sup>4</sup> from his study in the autoracemisation of an optically active ammonium compound in solution, has been induced to the notion that the configuration of ammonium compounds would be represented by a sphere as shown in Fig. III, in which the nitrogen atom is situated at the centre and the five atomic groups on the great circles at right angles to each other.

All those configurations founded on the same principle possess

1 Mem. Coll. Sci., Kyoto, 1, 303 (1916).

2 Ansichten u. Org. chem., 1878, p. 80.

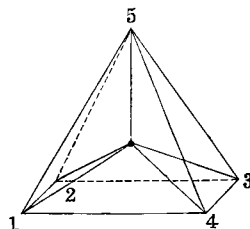
3 J. prak. Chem., 41, 291 (1890).

4 Z. Stereochem. d. funfw. Stick., 1907. p. 43.

the same defects and merits, so that none of them can explain the non-equivalence of the five valences of quinquivalent nitrogen or the non-existence of the isomerides of the inactive ammonium compounds.

4. The pyramidal configuration by Bischoff<sup>1</sup> represented by Fig. IV. and based upon Jones's<sup>2</sup> assumption on the mode of formation of ammonium compounds from amines stands in harmony with the decomposition and formation of the ammonium compounds, but not with their absorption spectra of the ultra violet rays and with the asymmetry of the molecule.

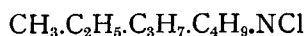
Fig. IV.



It is quite strange that we have not yet observed the existence of an optically active ammonium compound in nature; this may be ascribed to the specific character of the nitrogen atom which possesses no definite valency, changing from quinquivalence to trivalence or vice versa, and as consequence the autoracemisation of the optically active ammonium compounds naturally taking place.<sup>3</sup>

The attempts by various chemists to prepare the optically active ammonium compounds were successfully executed only in the compounds of the following types,  $\text{NRR}'\text{R}''\text{R}'''\text{X}$  and  $\text{NRR}'\text{R}''\text{XX}$ . They may be grouped as follows:

1. Methyl ethyl propyl isobutyl ammonium chloride,<sup>4</sup>



2. Methyl allyl phenyl benzyl ammonium iodide<sup>5</sup>



3. Methyl allyl tetrahydroisoquinolium iodide,<sup>6</sup>

1 Ber. D. chem. Ges., **23**, 1972 (1890).

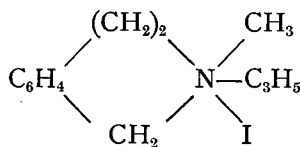
2 J. Chem. Soc., **87**, 1730 (1905)

3 Komatsu, Mem. Coll. Sci., Kyoto, **1**, 231 (1915); Pope and Harvey, J. Chem. Soc., **91**, 828 (1901).

4 Le Bel, Compt. rend., **112**, 724 (1891); **129**, 549 (1899).

5 Pope and Peachey. J. chem. Soc., **75**, 1127 (1899); **79**, 828 (1901); **101**, 519 (1912); Wedekind, Ber. D. chem. Ges., **32**, 722 (1899); **38**, 438 (1905); Z. phys. Chem., **45**, 235, (1903); Jones, J. Chem. Soc., **83**, 1418 (1903); **85**, 223 (1904); **87**, 1721 (1905); **89**, 280 (1906); **93**, 1790 (1908); Komatsu, Mem. Coll. Sci., Kyoto, **1**, 123 (1915); Wedekind und Fröhlich, Stereochem., 1907, p. 36; Reilly, J. Chem. Soc., **111**, 21 (1917).

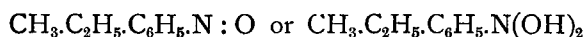
6 Wedekind., Ber. D. chem. Ges., **32**, 722 (1899); **38**, 1642 (1905); **40**, 4450 (1907); **41**, 456 (1908); **42**, 2138 (1909); **45**, 1293 (1912);



4. Methyl ethyl phenyl hydrazonium iodide,<sup>1</sup>

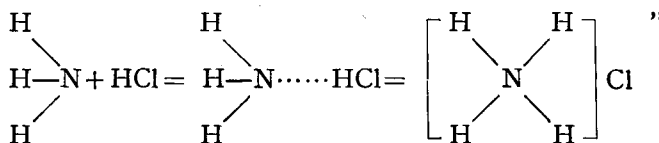


5. Methyl ethyl aniline oxide<sup>3</sup> or Methyl ethyl phenyl ammonium oxide,



The existence of each of these compounds in the optical antipodes not only suggests the non-equivalence of five valences of the nitrogen atom, but also gives us an assurance that the asymmetry of the molecule depends wholly upon the four groups attached to the nitrogen by the positive valence, the fifth so-called negative group exerting no influence whatever on it.

For explaining these facts Meisenheimer<sup>2</sup> has put forward an hypothesis about the configuration of ammonium compounds which seems to have originated from Werner's hypothesis.<sup>3</sup> He states "Das Ammoniak bindet zunächst den Wasserstoff der Salzsäure durch Nebenvalenz. Dan tritt Affinitätsausgleich ein, so daß schließlich alle vier Wasserstoffatome durch gleiche Affinitäts beträge, die aber geringer sind als eine volle Affinität, an den Stickstoff gebunden sind....." 'An den einzelnen Atomen des Komplexes  $\text{NH}_4$  sind noch bestimmte Affinitätsbeträge ungesättigt, die das Radikal  $\text{NH}_4$  nach außen hinzer Wirkung bringt, wodurch es Einwertig wird' "und so also den Säurerest bindet:



With regard to the configuration of ammonium compounds, he further states " Sämtliche fünf Radikale sind durch Hauptvalenz an

<sup>1</sup> Singh, J. Chem. Soc., **103**, 604 (1913); **105**, 1972 (1914).

<sup>2</sup> Meisenheimer, Ber. D. chem. Ges, **48**, 396 (1908); Lieb. Ann., **385**, 117 (1911).

<sup>3</sup> Lieb. Ann., **397**, 280 (1913).

<sup>4</sup> Lehrbuch d. Stereochemie, 1904, p. 310.

den Stickstoff gebunden, vier in einer inneren, eines in der äußeren Zone..... Der in der äußeren Zone stehende ebenfalls durch Hauptvalenz gebundene Säurerest nimmt, wie in tautomeren Substanzen—wenigstens in Lösung—keine festen plätzen und hat daher auf die Asymmetrie des Moleküle keine Einfluß."

Ammonium compounds with regard to their molecular asymmetry should bear close analogy to carbon compounds,<sup>1</sup> and comparing their absorption spectra, formation and other reactions with those of metal complexes,<sup>2</sup> one can not fail to admit that there is a great similarity. Hence, the author is of the same opinion with Werner and Meisenheimer in some respects with regard to the configuration of ammonium compounds.

The author's conception for the configuration of quaternary ammonium compounds is that the coordinate number of nitrogen is four, and the four atoms or atomic groups in the inner zone is supposed to be situated at four corners of a tetrahedron or on the surface of a sphere, i.e., the nitrogen atom is at the centre of a tetrahedron or sphere, and the four groups at its four corners.

*The negative atom or atomic group in the outer zone is attached to the nitrogen in one definite position as shown in Figs. V and VI.*

Fig. V.

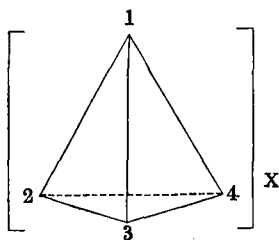
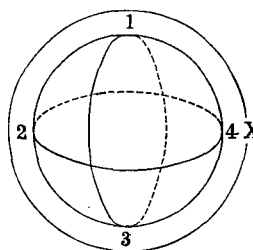


Fig. VI.



Its position in the outer zone may, therefore, depend upon the manner of formation of ammonium compounds and exerts an in-

1 Wedekind, Ber. D. chem. Ges., **36**, 1163, 3800 (1903); **38**, 1843 (1905); **42**, 303 (1909); Lieb. Ann. **401**, 326; **404**, 322 (1914); Scholtz, Ber. D. chem. Ges., **37**, 3627 (1904); **38**, 595, 1289 (1905); **40**, 685 (1907); Jones, J. Chem. Soc., **87**, 135 (1905); Aschan., Z. phys. Chem., **46**, 304 (1903); Mills and Bain, J. Chem. Soc., **105**, 64 (1914).

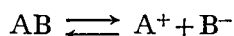
2 Werner, Lieb. Ann., 386, 1 (1912); Nicoloplos, Z. phys. Chem., **82**, 361 (1913); Shibata, J. Coll. Sci., Tokyo, **37**, 1 (1915); Compt. rend., **157**, 593. (1913); Komatsu, Mem. Coll. Sci., Kyoto, **1**, 303 (1916).



fluence upon the rotation of the compounds, but not upon the decomposition and other chemical and physical properties.

According to Werner and Meisenheimer's view for the configuration, the atom or atomic group in the outer zone would exert no influence upon the asymmetry of molecule, so that there exists no isomers of the different rotatory powers in the same ammonium compound. The author has, however, succeeded in isolating  $\alpha$  and  $\gamma$  active forms in methyl allyl phenyl benzyl ammonium compound<sup>1</sup>. By autoracemisation  $\alpha$  form was found to convert to the stable  $\gamma$  form<sup>2</sup>; so the author's opinion has now been definitely confirmed.

Applying the author's hypothesis to solution, it is evident that when the molecule AB dissociates into A and B there may still exist a kind of chemical affinity between them,<sup>3</sup> being supposed to be different from the Arrhenius electrolytic dissociation:



and so called dissociation degree is assumed to be dependent upon the strength of affinity between two particles or distance between them. Now the facts that the rotatory power of the ammonium salts of optically active acids<sup>4</sup>, being of a specific nature, has neither additive nor ionic properties well coincide with the author's view.

---

<sup>1</sup> Komatsu, Mem. Coll. Sci., Kyoto **1**, 123 (1915).

<sup>2</sup> Ibid., **1**, 231 (1915).

<sup>3</sup> Ibid., **1**, 234 (1915).

<sup>4</sup> Van't Hoff, Die Lagerung d. Atome im Raume. 1908, p. 75-92.