THE
ORGANIC CHEMISTRY
OF NITROGEN

BY

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NEW EDITION
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PREFACE

THE first edition of this book was published in 1910, and in 1922 Professor Sidgwick began to make plans for bringing out a revised edition. His intention was to ask chemists in Oxford to help him by revising individual chapters and to write the final text himself, making use of the information compiled by these collaborators. During 1932–3 he completed the first draft of Chapters I, III, VIII, and XII. His many duties, however, prevented the fulfilment of this plan and in the summer of 1934 we were entrusted with the task of rewriting the whole book and took over all the material which had been accumulated. We have revised each chapter anew, and the text as it stands is ours with the exception of two sections mentioned later. Our labours have been considerably lightened by the preliminary work carried out by the original collaborators whose names are given below. We alone are responsible for the opinions expressed, which differ in some details from those of the collaborators.

The plan of the book remains essentially the same as in the first edition. The intention is to give an account of the simpler organic compounds of nitrogen and to discuss some of the interesting problems which their properties and behaviour present, giving as far as is possible adequate explanation of the necessary physical background. We have thought it best to keep the discussion as close as possible to the experimental data and not to embark on any lengthy theoretical treatment of the facts. The book is inevitably longer than in its first edition because of the greater number of known facts. Two subjects discussed in that edition have been omitted, the derivatives of purine and the simpler alkaloids. The chief reason for the first of these omissions is that neither of us felt that his own knowledge of purine chemistry was adequate for a proper treatment of the subject, and for the second that descriptions of the alkaloids are to be found in other works in English and that the space so gained could be profitably devoted to a fuller description of the fundamental chemical properties of the simpler heterocyclic compounds. One of our chief difficulties has been to decide how much space should be allotted to the various classes of compounds. Not unnaturally we have given somewhat greater attention to the subjects where, because of our own knowledge, we have felt on surer ground.

Among those who have collaborated in collecting material mention must first be made of Mr. K. F. Armstrong who was killed in a ski-ing accident in Austria in January 1935. For the last six months of his life he had been collecting data for Chapters V and X, and he had also written valuable notes on the material compiled by others for Chapters IV and XVII. His death at the early age of 25 deprived us of one of the most valuable of our collaborators.

The following gentlemen have assisted by collecting material and in some cases by writing preliminary drafts for various chapters: Dr. J. C. Smith, Chapters XII and XV and the section on nitrophenols in Chapter VIII; Mr. D. Ll. Hammick, Chapters VII and VIII; Prof. J. M. Gulland, Chapter IV; Dr. S. G. P. Plant, Chapters XVII and XVIII; Dr. R. G. A. New, Chapter X, especially the section on isocyanides; Dr. E. Hope, Chapters XIII and XIV; Dr. F. E. King in preliminary work on Chapter V; Dr. F. M. Brewer, in preliminary work on Chapter I and in the beginning of the organization of the revised edition. Mr. Hammick has contributed the section on the molecular complexes of aromatic nitro compounds in Chapter VIII and Professor Sidgwick that on chelate *o*-nitrophenol derivatives in the same chapter; in the text their initials are appended to these articles.

Many of these gentlemen have helped by reading and criticizing various sections of the final text, and their comments have added greatly to its accuracy. Dr. A. Weissberger also gave great assistance in this way while he was in Oxford, particularly in Chapters IX, X, and XI. Professor R. Robinson was always willing to discuss difficult points and these discussions have been of great value especially for Chapters XII and XVII. Finally, Professor Sidgwick read almost the whole manuscript in its final form and wrote detailed critical notes on it; these have contributed largely towards clarity and accuracy in the text.

The references given are not intended to be complete. References to the early work can be found in Beilstein's *Handbuch* and Meyer and Jacobson's *Lehrbuch*. Those which appear are for the most part either to the more important papers or to the comparatively recent work which is not yet included in those two standard works. Our thanks are due to Mrs. T. W. J. Taylor who has spent much time in checking all the references with the original literature and in helping with proof-reading. The diagram on page 42 is taken from G. Wittig's *Stereochemie*, published by the Akademische Verlagsgesellschaft, Leipzig 1930.

T. W. J. T.
November 1936 W. B.

NOTE

Under present circumstances it has not been possible to make the many additions and alterations which would be required to bring the book up to date. The opportunity has been taken to correct errors and to make some minor modifications of the text. Part of the section on Molecular Complexes formed by aromatic nitro compounds (p. 261) has been rewritten by Mr. D. Ll. Hammick, and a note has been added on *cis*-azobenzene (p. 456).

In making these alterations it has not been possible to consult with Mr. T. W. J. Taylor who is away on War Service, and responsibility for them is mine.

W. B.

May 1942

ABBREVIATIONS

A = Ångström unit, 10^{-8} cm.
A, see footnote, page 107.
Ac = an acyl radical, such as acetyl, $CH_3 \cdot CO$.
Ar, Ar′ = an aromatic monovalent radical, such as tolyl, $CH_3 \cdot C_6H_4$.
Bz = benzyl, $C_6H_5 \cdot CH_2$.
D = Debye unit of electric moment, 10^{-18} electrostatic units.
Et = ethyl, C_2H_5.
M = an atom of a monovalent metal.
Me = methyl, CH_3.
R, R′, &c. = a monovalent organic group, except where otherwise described; usually an alkyl group.
R, see footnote, page 106.
X = a monovalent group; often an anion such as Cl^-.
ϕ = phenyl, C_6H_5.
[ ] indicates an ion, either kation or anion, except when used to indicate a concentration term in an equilibrium constant.

ABBREVIATIONS FOR TITLES OF JOURNALS

Ahrens' Sammlung. F. B. Ahrens' Sammlung chemischer und chemisch-technischer Vorträge.
Amer. Chem. J. American Chemical Journal.
Annalen. J. Liebig's Annalen der Chemie.
Anal. soc. españ. fís. quím. Anales de la sociedad española de física y química.
Ann. Chim. Annales de Chimie.
Ann. Chim. Phys. Annales de Chimie et de Physique.
Ann. Physik. Annalen der Physik.
Ann. Reports C. S. Annual Reports of the Progress of Chemistry; the Chemical Society.
Ann. Rev. Biochem. Annual Review of Biochemistry.
Arch. exp. Path. und Pharm. Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Pharm. Archiv der Pharmazie.
Arch. Sci. phys. nat. Archives des Sciences physiques et naturelles.
Arkiv f. Kemi. Arkiv för Kemi, Mineralogi och Geologi.
Atti R. Atti della Reale Accademia Nazionale dei Lincei.
Ber. Berichte der deutschen chemischen Gesellschaft.
Biochem. J. Biochemical Journal.
Biochem. Z. Biochemische Zeitschrift.
Bull. Acad. roy. Belg. Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Soc. chim. Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg. Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol. Bulletin de la Société de Chimie biologique.
Bur. Standards J. Bureau of Standards Journal of Research.
C.r. Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.

C.r. du Lab. Carlsberg. Comptes rendus des travaux du Laboratoire de Carlsberg.

Canad. J. Res. Canadian Journal of Research.

Chem. and Ind. Chemistry and Industry Review.

Chem. News. Chemical News.

Chem. Rev. Chemical Reviews.

D. R.-P. Deutsches Reichs-Patent.

Eng. Pat. English Patent.

Fried. P. Friedlaender's Fortschritte der Teerfarbenfabrikation.

Gazz. Gazzetta chimica italiana.

Helv. Chim. Acta. Helvetica Chimica Acta.

Ind. Eng. Chem. Industrial and Engineering Chemistry.

J. Amer. C. S. Journal of the American Chemical Society.

J. biol. Chem. Journal of biological Chemistry.

J. C. S. Journal of the Chemical Society.

J. Chem. Phys. Journal of Chemical Physics.

J. Gen. Chem. Russ. Journal of General Chemistry, Russia.

J. Gen. Physiol. Journal of General Physiology, Baltimore.

J. Ind. C. S. Journal of the Indian Chemical Society.

J. Phys. Chem. Journal of Physical Chemistry.

J. Physiol. Journal of Physiology.

J. pr. Chem. Journal für praktische Chemie.

J. Russ. Phys. Chem. Soc. Journal of the Physical and Chemical Society of Russia.

J.S.C.I. Journal of the Society of Chemical Industry.

J. Soc. Dyers and Colour. Journal of the Society of Dyers and Colourists.

Mem. Coll. Sci. Kyoto Imp. Univ. Memoirs of the College of Science, Kyoto Imperial University.

Mém. Poudres. Mémorial des Poudres.

Monats. Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.

Naturwiss. Naturwissenschaften.

Österr. bot. Z. Österreichische botanische Zeitschrift.

Pharm. J. Pharmaceutical Journal.

Phil. Trans. Philosophical Transactions of the Royal Society of London.

Phys. Review. Physical Review.

Phys. Z. Physikalische Zeitschrift.

Pogg. Ann. J. C. Poggendorff's Annalen der Physik und Chemie.

Proc. K. Akad. Wetensch. Amsterdam. Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings.

Proc. Nat. Acad. Sci. Proceedings of the National Academy of Sciences.

Proc. Roy. Soc. Proceedings of the Royal Society.

Quart. J. Physiol. Quarterly Journal of Experimental Physiology.

Rec. trav. chim. Recueil des travaux chimiques des Pays-Bas.

Rev. chim. ind. Revue de chimie industrielle.

S. African J. of Science. South African Journal of Science.

Sitz. Akad. Wiss. Wien. Sitzungsberichte der Akademie der Wissenschaften, Wien.

Trans. Faraday Soc. Transactions of the Faraday Society.

Trans. Roy. Soc. Canada. Transactions of the Royal Society of Canada.

Trans. Roy. Soc. Edin. Transactions of the Royal Society of Edinburgh.

Z. angew. Chem. Zeitschrift für angewandte Chemie.

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Z. anorg. Chem. Zeitschrift für anorganische und allgemeine Chemie.
Z. Biologie. Zeitschrift für Biologie.
Z. Elektrochem. Zeitschrift für Elektrochemie.
Z. f. Chem. Zeitschrift für Chemie.
Z. ges. Schiess- u. Sprengstoffw. Zeitschrift für das gesamte Schiess- und Sprengstoffwesen.
Z. Krist. Zeitschrift für Kristallographie.
Z. phys. Chem. Zeitschrift für physikalische Chemie.
Z. physiol. Chem. Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. Wiss. Photograph. Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Zent. Chemisches Zentralblatt.

INTRODUCTION

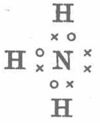
By N. V. SIDGWICK

THE NITROGEN ATOM

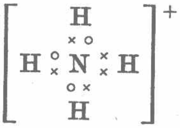
NEXT to carbon, nitrogen is the most important element in organic chemistry for the variety and interest of the compounds into which it enters. Some remarks about the general characteristics of the element may conveniently precede the discussion of its organic compounds.

Nitrogen, atomic number 7, is the lightest element of the fifth periodic group, and so has 5 valency electrons. In nearly all its compounds it increases this number to 8. It cannot do this by direct addition, with the formation of a trivalent anion N^{---}, because this triple charge would cause so great a deformation of the orbits by the cation that the electrovalency would pass over into a covalency.[1] Hence it is by the sharing of electrons—by the formation of covalencies—that the necessary electrons are gained. In this way two normal states of the nitrogen atom can arise, (1) trivalent and tricovalent, as in NH_3, with a valency group of 8 electrons, 6 shared (I), and (2) 4-covalent with a fully shared octet, in which the nitrogen, since it uses all its 5 valency electrons, is pentavalent. The fourth covalency can be established by co-ordination of the lone pair of the trivalent atom acting as a donor, and the acceptor may either be a positive ion as H^+ (or a univalent radical as methyl, losing an electron on combination), in which case a positive ammonium ion is formed (II a), or the acceptor may be a neutral divalent atom such as oxygen, when the product is a neutral molecule (II b).

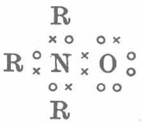
I.



II a.



II b.



A 5-covalent state, like that of phosphorus in the pentafluoride PF_5, is impossible for nitrogen, because the elements in the first short period are limited in their covalency to 4, as was first pointed out by Werner (see p. 32).

In addition to these normal states, we find a certain number of compounds of nitrogen in which there is one electron more (or one less) in the molecule than is required for the completion of the octet, the resulting molecule having an odd number of electrons (the 'odd molecules' of G. N. Lewis). The most familiar of these are the two oxides nitric oxide NO and the monomeric form of nitrogen peroxide NO_2; a series of organic derivatives of these types have also been prepared (see p. 165 and 388).

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[1] It is possible that this ion may occur in some inorganic nitrides.

These molecules are found to be paramagnetic, as we should expect (all ordinary organic substances are diamagnetic), and the nitrogen always tends to revert to a normal state of combination. The state of linkage in such molecules as these cannot be expressed in the ordinary symbols, and the occurrence of these unusual forms of attachment can in fact only be understood in the light of the theory of resonance discussed in the next section (p. xv).

The heats of formation of the links of nitrogen to other atoms are of importance as determining the thermodynamic stability of its compounds. Their values are in many cases approximately known, and do not vary greatly (apart from the occurrence of resonance) with changes in the other parts of the molecule. The values required are those of the formation of the link in the gaseous state from the component atoms, and hence involve a knowledge of the heats of atomization of the elements concerned. In the list below that of carbon is assumed to be 169 and that of nitrogen 84·5 kcals.[1]

Heats of Formation of Links from Atoms

(Kcals. per gm. mol. in the gas at 25°.)

N—H 83   N—F 69   N—Cl 39   N—O 49 ?

	Abs.	Rel.		Abs.	Rel.		Abs.	Rel.	Mean
N—N	23	1	C—C	80·5	1	C—N	59	1	51·8
N=N	61	2·7	C=C	142	1·7	C=N	121·5	2·1	101·5
N≡N	169	7·4	C≡C	189·5	2·4	C≡N	180	3·1	179·3

The most important conclusion which emerges from these figures is the very different effects of multiplicity on the heat of formation in carbon and in nitrogen. As will be seen, the heat value rises less rapidly than the multiplicity with C—C, and much more rapidly with N—N; with the links of carbon to nitrogen the rise is almost exactly proportional to the number of links; in fact the value is in every case very nearly the mean of those for C—C and N—N, as the last column in the table shows. This corresponds to a fundamental difference in behaviour between carbon and nitrogen. In a carbon chain the presence of a multiple link is, as is well known, a sign of weakness: the chain is likely to break between these two atoms. A double link between two nitrogen atoms, on the contrary, is a sign of strength: the chain never breaks at that point, except on reduction with hydrogen, for which, as the heat values show, nitrogen has a peculiarly strong affinity; the tendency is for the double nitrogen link to turn into a triple link, i.e. for the —N=N— group to separate as nitrogen gas. This is what happens with the diazo compounds (both aromatic (p. 404) and aliphatic (p. 352)), and the azides (p. 368) and the azo-compounds (p. 432).

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[1] These must replace the incorrect values of 150 for carbon and 104 for nitrogen previously assumed, e.g. in my *Covalent Link*, 1933; see for nitrogen R. S. Mulliken, *Phys. Rev.* 1934, ii, **46**, 144; G. Herzberg and H. Sponer, *Z. phys. Chem.* 1934, B, **26**, 1; for carbon E. C. Baughan, *Nature*, 1941, **147**, 542; G. J. Kynch and W. G. Penney, *Proc. Roy. Soc.* 1941, **179**, 214.

Even a singly linked pair of nitrogen atoms often breaks off in the form of elementary nitrogen, as with phenylhydrazine on treatment with copper sulphate (p. 382).

Since the heat of formation of the link between carbon and nitrogen is so closely proportional to the multiplicity, we should expect the stability of the single, double, and treble links to be much the same. The observed facts do not quite agree with this. The triple C≡N link is not much less stable than the single, but in certain reactions, especially hydrolysis, the double link C=N, as in the imines, the Schiff bases, and the anils (p. 65), is much less stable than either.[1]

RESONANCE

[This subject is the main theme of L. Pauling's *The Nature of the Chemical Bond* (Cornell University Press, 1939). Among the most important papers are Pauling, *J. Amer. C. S.* 1932, **54**, 988, 3570 (covalent and electrovalent links): idem, *Proc. Nat. Acad. Sci.* 1932, **18**, 293, 498 (interatomic distances): Pauling and D. M. Yost, ibid. 414: Pauling and J. Sherman, *J. Chem. Phys.* 1933, **1**, 606 (heats of formation): Pauling and G. W. Wheland, ibid. 362: Pauling and J. Sherman, ibid. 679 (application to aromatic and hydroaromatic compounds): G. W. Wheland, ibid. 731 (keto-enols): L. O. Brockway and L. Pauling, *Proc. Nat. Acad. Sci.* 1933, **19**, 860 (organic azides): L. E. Sutton, *Trans. Faraday Soc.* 1934, **30**, 801 (dipole moments and resonance). See further C. K. Ingold, *Chem. Rev.* 1934, **15**, 225 (resonance and organic reactivity).]

The conception of resonance is the most important development which structural chemistry has had since it was extended to three dimensions by van 't Hoff in 1874. It is a result of the application of wave-mechanics, and could not have been deduced from classical dynamics; but its essential conclusions can be stated very simply. If a molecule can have two or more different structures in the ordinary organic sense of the term, then under certain conditions its actual state is neither one nor the other, but something intermediate between the two, which partakes to some extent of the properties of both, but cannot be expressed in the usual structural symbols. The molecule is then said to exhibit resonance, and to be a resonance-hybrid of the two or more structures.

The conditions for resonance to be possible between two structures are these: I. The relative positions of the atoms in space must be nearly the same in both. II. The two must not differ too greatly in stability, or, in other words, both formulae must be reasonably probable. III. The number of paired electrons must be the same in both; this last condition is practically always fulfilled, so long as we are not dealing with 'odd molecules'. The results of the resonance are the following: 1. The molecule has to some extent the properties of each constituent structure, though not necessarily to the same extent, the more stable form predominating. 2. The hybrid has a smaller energy content (a greater stability and heat of formation, a smaller heat of combustion) than either of the two structures. 3. The distances between the atoms are rather smaller than the normal. Of these effects the last is of small importance from the point of view of the reactivity and similar properties, but is very useful in detecting the occurrence of the phenomenon. The second is the most important of all, because it implies that resonance must always occur whenever it is possible, and also that its occurrence must always increase the stability of the molecule.

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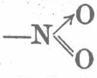
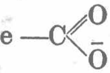
[1] The value given above for the C=N link is obtained from the heat of combustion of the isocyanates R—N=C=O, using the value (181 kcals.) for the C=O link derived from carbon dioxide; this would seem to make a reasonable allowance for resonance.

Resonance must be clearly distinguished from tautomerism. Both imply that we find only one compound when we expect on the structural theory to have two, but the resonance hybrid differs in that (1) it is one substance and not a mixture of two, (2) it can only occur when the two structures involve nearly the same positions of the atoms in space (so that it is impossible, for example, with the structures HCN and HNC), and (3) it must always be more stable than either of the two forms.

As an example where the resonance has been established by experimental tests of two kinds we may take carbon dioxide. This has three possible structures, the last two being identical. If we may assume that the length and the heat of formation of a co-ordinate link are the same as those of a normal covalency, the heats of formation of the three forms are nearly the same, since the values for C—O links are nearly proportional to the multiplicity. They are also all linear molecules, and the distances vary only to the small extent required by the change in multiplicity. Thus the essential conditions of resonance are satisfied, and we should expect it to occur. If it does so, the heat of formation of carbon dioxide should be greater, and the lengths of the links less, than corresponds to the structure O=C=O. That this is so is shown by the values in the following table; the observed C—O distance is 1·15 A instead of the normal C=O length of 1·28 A[1] and the heat of formation is 32 kcals. greater than that calculated from the value for a carbonyl group in aldehydes and ketones[2]

	$O=C=O$	$O\leftarrow C\overset{\leftarrow}{\equiv}O$	$O\overset{\rightarrow}{\equiv}C\rightarrow O$	Obs.
Distance, A.	1·28 1·28	1·43 1·13	1·13 1·43	
	2·56	2·56	2·56	2·30
Heat of Formation from atoms, kcals.	367	*ca* 370	*ca* 370	399

Familiar examples of resonance are afforded by the symmetry of the  $—N\begin{smallmatrix}\nearrow O\\ \searrow\!\!\!\searrow O\end{smallmatrix}$ group (indicated by the dipole moments), of the  $—C\begin{smallmatrix}\nearrow\!\!\!\nearrow O\\ \searrow \bar{O}\end{smallmatrix}$ ion, and of the NO_3' and CO_3'' ions. The crystallographic evidence shows that the last two are plane structures, as is required by the tetrahedral theory for the formulae

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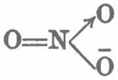
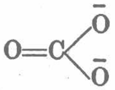
[1] L. Pauling, *Proc. Nat. Acad. Sci.* 1932, 18, 293.

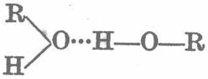
[2] L. Pauling and D. M. Yost ibid. 414; L. Pauling and J. Sherman, *J. Chem. Phys.* 1933, 1, 606.





but further, that the three oxygen atoms are at the points of an equilateral triangle, with the nitrogen or the carbon at the centre. This implies a resonance, with the double link not localized on any particular oxygen atom. Here too we find the characteristic shortening of the link.[1]

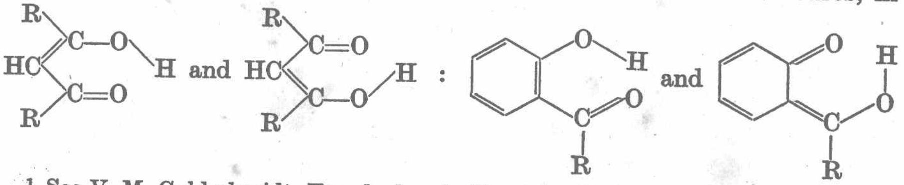
The applications of the theory are numerous and important. It provides the physical support for the theories of organic reactivity developed by Lapworth, Robinson, Ingold, and others, and it elucidates the properties of many important groups of compounds, such as the simple free radicals (p. 390), the triphenylmethane dyes (p. 82), and the cyanine dyes (p. 561); it is of especial value in interpreting the behaviour of aromatic systems (pp. 488, 496). But there is one phenomenon of special interest which is explained by resonance and, as far as we can see, by resonance alone. This is the so-called co-ordinated or dicovalent hydrogen. For some years it has been recognized that under certain conditions a hydrogen atom is able to link two other atoms together, as in the association of hydroxylic compounds and the formation of the F_2H anion.



$[F—H\cdots F]$

It was originally assumed that the hydrogen acted as the acceptor in a co-ordinate link A:H:B, having four shared electrons. Subsequent developments, while they have made it increasingly certain that hydrogen can act as a linking atom[2] have shown that this mechanism is impossible. It would be necessary for two of the four shared electrons to be in the second quantum group, and they would not be held firmly enough to account for the stability of the link. We therefore have to find some other mechanism for the link, and this is provided by the theory of resonance.

We can distinguish two sets of conditions under which this link occurs; firstly when it leads to the formation of a ring (chelate compounds), and secondly where the product is an open chain (association of hydroxylic compounds). Examples of chelate compounds are the β-keto-enols and the *o*-aldehydo-phenols. Here we have the two resonance structures, in



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[1] See V. M. Goldschmidt, Freudenberg's *Stereochemie*, 1933, p. 50.

[2] It has even been found possible to determine the length of the link, that is the distance between the nuclei of the oxygen or fluorine atoms in O—H···O and F—H···F, which is about 2·5 A: see W. H. Zachariasen, *J. Chem. Phys.* 1933, **1**, 634; J. West, *Z. Krist.* 1930, **74**, 306.

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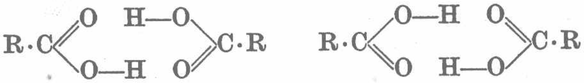
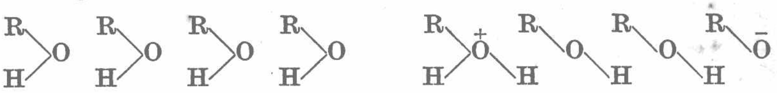
one of which the hydrogen is attached to one of the oxygens, and in the other to the other. The strain in a 6-ring with two double links is very small, so that the same position of the atoms fits either structure. This mechanism explains the fact that two isomeric enols of this type have never been isolated. We can also see why the tendency to chelation practically disappears when the β-keto-enols are reduced to β-keto-alcohols, $R \cdot CH(OH) \cdot CH_2 \cdot CO \cdot R$, since the migration of the double link is no longer possible. In the *o*-phenol derivatives, such as the aldehydes and nitrophenols (p. 268) we have to assume that the aromatic ring in the second structure is *o*-quinonoid: interesting evidence on this point has been given by W. Baker.[1]

Sometimes this ring-formation occurs by the combination of two molecules, as with the carboxylic acids.[2] These compounds can be shown to polymerize readily to double molecules but no further.



The association of the simpler hydroxylic compounds—water, alcohols, phenols—giving chains and not rings must be explained in some other way. Molecules of this kind are known to associate less readily in dilute solution than carboxylic acids or oximes, but with increasing concentration the polymerization increases indefinitely, and can go far beyond the dimeric stage.[3] This must occur through the formation of oxonium ions:



The length of the chain can be extended indefinitely, and it will in fact be determined by the balance between the resonance energy and the thermal agitation. It must be realized that the resonance depends on the atoms retaining their positions. Accordingly the RH_2O^+ and RO^- ions are not free to move so long as the resonance persists; the whole chain forms a 'zwitterion' and cannot contribute to the conductivity, which will be due only to those ions which are displaced from the chain by thermal agitation.

Co-ordination of Hydrogen attached to Nitrogen

The most familiar and important case of 'co-ordinated' hydrogen is that in which it links two oxygen atoms. The power of a hydrogen to link two other atoms in this way is wholly dependent on the nature of these atoms: it is almost nothing in C—H, small in N—H, larger in O—H, and still larger in F—H. When we pass from the first period to the second, it almost vanishes, being practically zero in P—H and S—H, and very small in Cl—H.

---

[1] *J.C.S.* 1934, 1684; Baker and O. M. Lothian, ibid. 1935, 628; 1936, 274; W. Baker, *Nature*, 1936, **137**, 236.

[2] See *Ann. Reports C. S.* 1933, **30**, 115.

[3] See for example F. S. Brown and C. R. Bury, *J. Phys. Chem.* 1926, **30**, 694.

The tendency of hydrogen attached to nitrogen to form a further link is small, and is almost confined to one kind of grouping, which is, however, of considerable importance. This is the formation of an undissociated hydroxide from an amine and water. It has been shown (see p. 31) that the base, whether this is ammonia or a primary, secondary, or tertiary alkylamine, is present in aqueous solution to a considerable extent as the undissociated hydroxide, which may be written $R_3N—H\cdots O—H$. That the hydroxyl is attached through the amine hydrogen is shown by the fact that a quaternary hydroxide cannot form such a link and is accordingly a strong electrolyte. The linkage must be due to resonance between two forms, in one of which the linking hydrogen is attached to the nitrogen, and in the other to the oxygen of the hydroxyl; this gives us the very simple picture

$$R_3N—H\cdot\ [OH] \qquad R_3N\ \ H—OH.$$

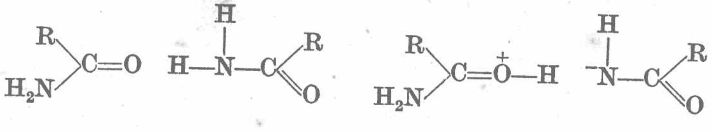
It must be remembered that here, as in the associated alcohols described above, the R_3N and H—OH molecules are not free to move so long as the resonance with its accompanying gain of energy is maintained, and hence the amine molecules which are bound in this way to the water will not be soluble in a hydrocarbon solvent; they will thus appear, in the partition measurements of Moore and Winmill (p. 30), as a separate molecular species from the free R_3N.

Under any other conditions than these the power of the N—H hydrogen of forming a further link is very small. Ammonia itself is undoubtedly associated, as is proved by the absorption in the infra-red, but only to a very small extent. This must involve the structures

$$H_3N\ \ H—NH_2 \qquad H_3\overset{+}{N}—H\ \ \overset{-}{N}H_2.$$

Now the H_4N^+ ion is at least as stable as H_3O^+, and so the fact that ammonia is far less associated than water must be due to the anion $\overset{-}{N}H_2$ being much less stable than $\overset{-}{O}H$.

The linkage of nitrogen to oxygen through hydrogen can no doubt occur to some extent even when the ionic charges are not as favourable as in the ammonium hydroxides. This presumably explains the association of amides.



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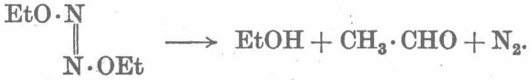
CHAPTER I

ESTERS OF HYPONITROUS, NITROUS, AND NITRIC ACIDS

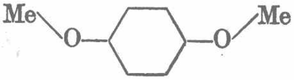
ESTERS OF HYPONITROUS ACID, $R\cdot O\cdot N{:}N\cdot O\cdot R$

THE esters of hyponitrous acid have been prepared by the action of alkyl iodides on pure silver hyponitrite,[1] but have been little investigated. The simpler esters are colourless liquids, insoluble in water, which cannot be distilled without decomposition, even under reduced pressure. The benzyl ester is a solid melting at 48–49° which can be crystallized from a mixture of ether and light petroleum. The esters all show a normal molecular weight in benzene solution. They are unstable and decompose on standing at room temperature; the decomposition is faster at higher temperatures and on rapid heating they detonate with a somewhat violent explosion. In presence of water the hyponitrous esters are rapidly decomposed at temperatures above 40°, nitrogen being evolved:



$$\begin{array}{l}\mathrm{EtO\cdot N}\\ \qquad\| \\ \qquad\mathrm{N\cdot OEt}\end{array} \longrightarrow \mathrm{EtOH} + \mathrm{CH_3\cdot CHO} + \mathrm{N_2}.$$

The constitution of these esters is shown by the fact that on reduction no amine can be detected; hence the alkyl groups cannot be attached to nitrogen. Since the molecule contains doubly linked nitrogen atoms, two geometrically isomeric forms of an ester might exist, just as geometrical isomerism is found in the diazohydrates and diazocyanides (see p. 417); these would correspond to *cis* and *trans* arrangements of the alkoxy groups about the two nitrogen atoms. No such isomerism has, however, been observed. The electric moment of the ethyl ester is 1·5 D and that of the benzyl ester 0·4 D.[2] These comparatively small values suggest that the esters exist in the *trans* configuration which is shown in the equation above. In spite of the fact that this formula, as written, implies that the molecule has a centre of symmetry, it is not to be expected that it would have zero moment, because of the free rotation about the oxygen valencies which do not lie in one straight line. The case is similar to that of the dimethyl ether of quinol



which has a moment of 1·74 D. In this compound the methyl groups do not lie on the line joining the centre of the ring to the oxygen atoms and

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[1] W. Zorn, *Ber.* 1878, **11**, 1630; A. Hantzsch and L. Kaufmann, *Annalen*, 1896, **292**, 329; J. R. Partington and C. C. Shah, *J.C.S.* 1932, 2593.

[2] E. C. E. Hunter and J. R. Partington, ibid. 1933, 309.

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