

DIRECTED VALENCE IN POLYATOMIC MOLECULES

BY J. C. SLATER

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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ABSTRACT

The interactions of atoms in polyatomic molecules are described qualitatively. Particular attention is paid to atoms of the types of F, O, N, C, where the valences come from p electrons. Directional effects are discussed, namely that the two valences of O, and the three of N, tend to be mutually at right angles, and the four of C have tetrahedral symmetry. Numerous examples are given, from the structure of metals and of organic and inorganic compounds. Mathematical treatment is postponed until a later paper.

IT HAS already been noticed by Born¹ that the method applied by the writer to the problem of complex atomic spectra is equally adaptable to molecular structure. The writer² has used the method in one problem of atomic interaction, the problem of cohesive forces in univalent metals. When applied to molecular problems in general, however, it yields not only the familiar results for diatomic molecules, but also information regarding valence in polyatomic molecules, particularly in the matter of directional properties, which seems to be new and which is capable of correlating a good deal of experimental material. In this paper, we give the results of the discussion in a qualitative way, postponing mathematical justification to a later paper.

The general ideas described in the paper were outlined in an informal talk at the Washington meeting of the American Physical Society last April, and I wish to thank several members of the society for valuable discussion at that time. I also wish to acknowledge valuable assistance and suggestions from several of my colleagues, particularly Dr. Warren, Dr. Ashdown, and Dr. Scatchard.

Two atoms containing all their electrons in closed shells repel each other. But if each atom has one wave function containing only one electron, rather than two of opposite spins, attraction is possible. This actually occurs if the spins of the electrons in question in the two atoms are oppositely directed. The attraction pulls the atoms together until the wave functions from which electrons are missing overlap as much as possible, when equilibrium occurs. In consequence of resonance, the charge concentrates at the place where the functions are overlapping, and in an approximate way we may consider that the two electrons, of opposite spin, spending their time in this region, form a closed shell. This is a homopolar valence bond, and two electrons forming such a bond are inactive in forming further bonds, just as if they were in closed shells within a single atom.

¹ M. Born, *Zeits. f. Physik* **64**, 729 (1930).

² J. C. Slater, *Phys. Rev.* **35**, 509 (1930).

The simplest and most familiar example of a single valence bond is found in H_2 ,³ where each atom contains a single $1s$ electron, so that the $1s$ shell is not completed, and if the spins are oppositely directed, the electrons are shared and form a molecule. But almost equally simple is, for example, I_2 . Here each atom lacks a single p electron from its outer shell. If the remaining electron in that particular p wave function in one atom has a spin opposite to that in the other, there will be attraction, which will proceed until the two wave functions overlap as much as possible. We meet at once the question, how does the degeneracy of the p shell affect the problem. And we can answer definitely from perfectly general considerations.

To get the lowest possible energy, we wish in a rough way the greatest possible overlapping of the p functions from the two atoms. This demands first that each of these functions be as concentrated as possible. Now the wave functions corresponding to the three p levels, in the ordinary axial system of coordinates, can be written

$$\begin{aligned} p^+ &: (x + iy) f(r) \\ p^0 &: z f(r) \\ p^- &: (x - iy) f(r). \end{aligned}$$

The charge densities corresponding to these are

$$\begin{aligned} p^+ &: (x^2 + y^2) f^2(r) \\ p^0 &: z^2 f^2(r) \\ p^- &: (x^2 + y^2) f^2(r). \end{aligned}$$

As shown in Fig. 1, made by a very ingenious method by Dr. Langer, the first and third are great in the x - y plane, in a sort of ring-shaped region; the second

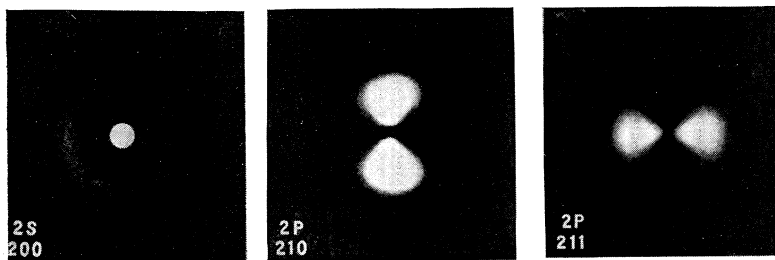


Fig. 1. Charge distribution of p^+ and p_0 , with s for comparison.
I am indebted to Dr. Langer for this photograph.

is great along the z axis, and is more concentrated than the others. But we are allowed to use any three orthogonal linear combinations of these functions. If we take $(r \cdot u_1) f(r)$, $(r \cdot u_2) f(r)$, $(r \cdot u_3) f(r)$, when u_1 , u_2 , u_3 are three orthogonal unit vectors, these functions will be great, respectively, along the

³ Heitler and London, Zeits. f. Physik **44**, 455 (1927).

axes of these three vectors, and each will be as concentrated as the p_0 before. These functions evidently give as concentrated a density as we can get, and hence are most suitable for use in discussing binding.

Let us now consider our I_2 molecule. We take the vector u_1 in each atom as the vector pointing toward the other atom. Then plainly the functions $(r \cdot u_1) f(r)$ for the two atoms, since they correspond to distributions pointing along the line of centers, and hence stretching out toward the other atom, can overlap. The other functions, on the other hand, are large in the planes normal to the line of centers, and do not overlap appreciably. We can visualize the atoms as the hubs of two wheels connected by an axle. The functions which overlap are extending along the axle, the others along the spokes of the two wheels. For binding, then, we assume an electron missing from this function $(r \cdot u_1) f(r)$ in each atom, and we can be confident that in this way we shall get the most stable molecule. In the usual description, if the z axis is taken as the axis of the molecule and at the same time the axis for axial wave functions for the electrons, an electron with function p_0 is missing from each atom. This coincides with the conventional description of this case.

Next let us consider an atom which lacks two electrons of having a complete shell, as for example O. Suppose we have another atom, as H, which can be bound to it. We choose our vectors u_1, u_2, u_3 so that one of them, say u_1 , points along the line from O to H. Then by the previous argument we must have one electron missing from the state which we may symbolize by u_1 , to form the bond with the H. The other missing electron must then be lacking from either the state u_2 or u_3 , and hence must have its density along the direction at right angles to the line joining the O and H. A second hydrogen attempting to become bound to form a water molecule, would move so that its charge would overlap in place of this missing one. It would then take up a position so that the lines joining the centers of the oxygen and the two hydrogen atoms would form right angles. Of course, the interactions between the two hydrogen atoms would modify this; it is difficult to say in which direction. But in a general way we should expect a triangular model, as is shown in Fig. 2, and that of course is observed.

The same sort of argument would indicate that the two valences of a divalent atom like oxygen should always be at right angles, and we can obtain many actual examples of this. The atoms of this sort are O, S, Se, Te. In the elements Se and Te in the solid state the atoms form chains of an interesting helical form, as shown in Fig. 3, so that if we look along the axis of the helix every third atom lies in a corresponding position. But just such a spiral is formed if atoms are arranged in a chain with the lines joining successive atoms making right angles with each other, these lines pointing in succession along the x, y, z, x, y, z, \dots , axes, which is the structure which our theory would suggest. Another illustration, less definite, is furnished by the crystal structure of the silicates. These are presumably in general ionic compounds. But some features of them resemble valence compounds: each silicon is surrounded by four oxygens, suggesting the valence of four and tetrahedral structure which we shall discuss in a later paragraph; and where an

oxygen is shared between tetrahedra, is shared by two only, as if it had just two valences for the two silicons. These features are both illustrated in Fig. 4. Now it is observed that in such a shared oxygen, the lines joining the oxygen to the silicons always form an angle with each other, as if there were

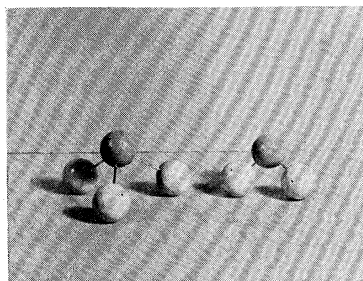


Fig. 2.

Fig. 2. NH_3 and H_2O . The angles here, and in the other figures, are taken to be just 90° , rather than adjusted to agree with experiment.

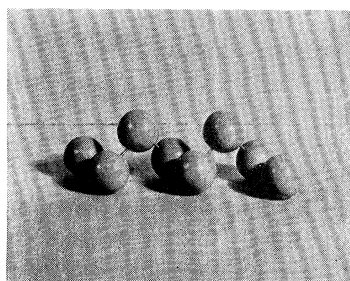


Fig. 3.

Fig. 3. Chain of atoms from Te. The actual chain continues indefinitely in both directions. The crystal is made of many chains packed together parallel to each other.

valences which tended to be at right angles to each other, rather than being parallel as one would otherwise expect.

The trivalent atoms, N, P, As, Sb, Bi, can be discussed by just the same principles: their three valences tend to be mutually at right angles, one elec-

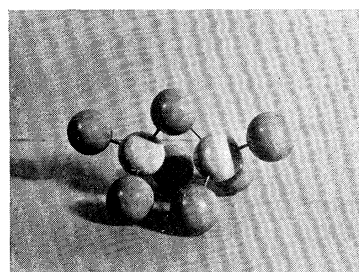


Fig. 4.

Fig. 4. $(\text{Si}_2\text{O}_7)^{-6}$ group from a silicate. The lighter atoms represent Si. Two tetrahedra are joined by sharing an O. In the actual case, the valences of this shared O are more nearly parallel than we have shown.

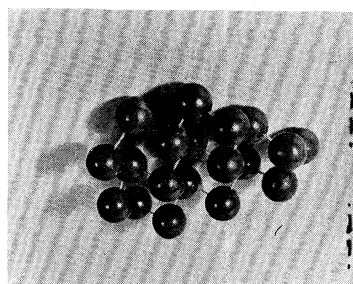


Fig. 5.

Fig. 5. Sheet of atoms from Bi. This consists of two layers of atoms, each atom being joined to three neighbors in the other sheet. The whole crystal consists of piles of these sheets.

tron being shared from each of the three functions with the factors $(r \cdot u_1)$, $(r \cdot u_2)$, $(r \cdot u_3)$. The most obvious example is ammonia, NH_3 , which has the pyramidal structure which we should expect from this model, as is shown in Fig. 2. Then in the metals, As, Sb, Bi, we find good illustrations of the princi-

ple. The atoms in these metals form plates, which appear, when we look down on them, like hexagonal lattices, each atom being surrounded by three others symmetrically placed. But really alternate atoms are displaced above or below the plane, as shown in Fig. 5, so that each atom above the plane is at the apex of a pyramid whose base is formed by three atoms below the plane, and vice versa; and the three lines joining an atom with its neighbors are very nearly at right angles. The whole crystal is formed by piling these plates together in such a way as to approximate a simple cubic lattice.

Other examples can be found in organic compounds containing nitrogen, in which the nitrogen is connected to something else by a double bond. In the oximes, as shown in Fig. 6, it is connected in this way to a carbon atom; in the azo compounds as in Fig. 7, to another nitrogen. The double bond we visualize simply as the sharing of two electrons, so that the two bonds and the center of the atom determine a plane. The third valence of the nitrogen

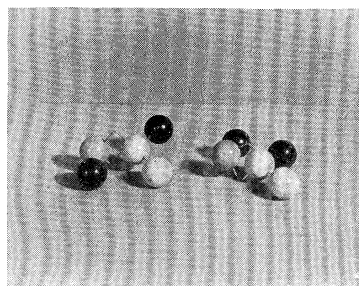


Fig. 6.

Fig. 6. Two isomeric forms of an oxime compound. A nitrogen and carbon are joined by a double bond. The two forms arise from the two possible orientations of the third valence of the nitrogen.

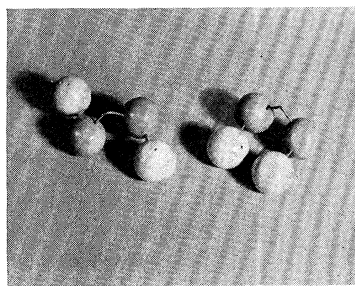


Fig. 7.

Fig. 7. Two isomeric forms of an azo compound. Two nitrogens are joined by a double bond.

should then, according to our picture, be at right angles to this plane, but it could point out in either of the two normal directions. If the rest of the molecule were not symmetrical about this plane, we should then expect two forms of the molecule, depending on which normal were chosen; and as a matter of fact, both these groups of compounds show isomerism which is attributed to just this sort of effect.

The tetravalent atoms, C, Si, Ge, Sn, Pb, demand a different treatment. If we assume that four electrons are removed from the group of six p 's, this leaves none in one of the three wave functions, and one each in the remaining two. Thus there are two electrons to be shared, as in O, and we have divalent atoms as we observe for example in CO. But to obtain a valence of four, we must plainly have only three p 's removed, leaving one electron each in these states; and the other missing electron must then be an s . This latter, having a spherical distribution of charge, has no directional properties. Thus in CH_4 , for example, we should tentatively expect that the three hydrogens attached

to p valences would form a pyramid, as in NH_3 , and the remaining hydrogen, bound to an s , and free to wander, would set itself opposite the apex of the pyramid to avoid the others, forming a rough tetrahedron. This would not be a symmetrical tetrahedron, however; and by a slight change in the conditions we can arrive at a really symmetrical one, which would undoubtedly have a lower energy, and which we consider to be the real form for a tetra-valent compound.

To arrive at this symmetrical arrangement, we set up four linear combinations of the three p wave functions and the one s function, having a tetrahedral symmetry. We take four unit vectors, u_1, u_2, u_3, u_4 , pointing to the four corners of a regular tetrahedron. Then the four functions $(r \cdot u_1) f(r), \dots, (r \cdot u_4) f(r)$ are, as we have seen, linear combinations of the three p functions, but of course they are not orthogonal. If however we take the s wave function, say $\phi(r)$, we can form combinations $(r \cdot u_1) f(r) + \alpha\phi(r), \dots, (r \cdot u_4) f(r) + \alpha\phi(r)$, where α is a parameter, and we can choose α to make the four

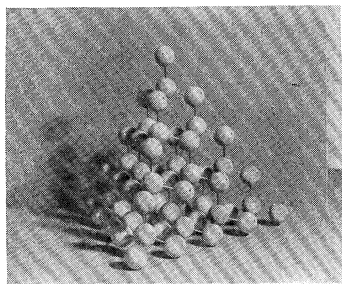


Fig. 8. Diamond lattice.

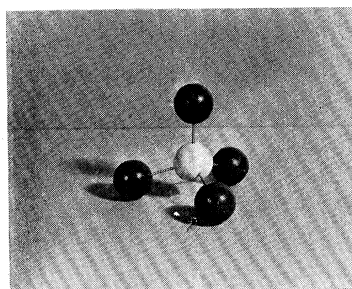


Fig. 9. CH_4 .

functions orthogonal. These are then the required tetrahedral wave functions. The density of each one is great along one of the axes of a regular tetrahedron; the addition of the s function results in having the density much larger in one direction than in the opposite one. If now each of these wave functions lacks one electron, and other atoms share with the remaining ones, they will take up a tetrahedral arrangement about the central atom.

The tetrahedral structure for the valence of C and the other atoms of this group is too well known to require extensive comment; a very great number of observations of the organic chemists have led to it. But we may mention a few examples. The solids as diamond, forms of Pb and Si, form the diamond lattice shown in Fig. 8, in which each atom is surrounded by four others in tetrahedral arrangement. The gas CH_4 , shown in Fig. 9, is undoubtedly tetrahedral, as shown by the absence of electric moment. The double carbon bond is explained very easily by the sharing of two electrons, meaning that two tetrahedra join by an edge. The remaining four valences then all lie in a plane, as shown in Fig. 10, and the isomerism of the derivatives of ethylene, $\text{H}_2\text{C}=\text{CH}_2$, is readily explained: given two unlike radicals attached to each atom, there will be two different compounds depending on the two possible

assignments of one pair to the two electrons of the corresponding atom. This explanation seems much more convincing than the ingenious theory of Hückel,⁴ based wholly on p electron valence.

The weakness of Hückel's theory is that he does not consider carefully the nature of the other bonds than the double one, and hence does not notice the fact which we point out, that the s valence must be combined with the p 's to obtain a symmetrical arrangement. If one followed his argument through, each of the carbons in ethylene would have one p valence and one s free to join to hydrogens, and the latter would then hardly be equivalent.

Similarly the triple bond would correspond to the sharing of a whole face of two tetrahedra. The remaining valences would then point out along the line of centers, so that acetylene, $\text{HC}\equiv\text{CH}$, shown in Fig. 11, should be a linear molecule, as is observed from its lack of dipole moment.

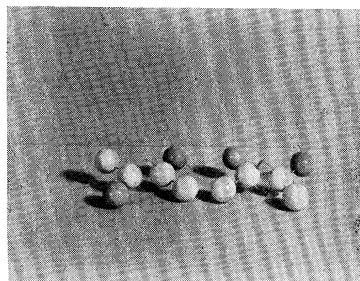


Fig. 10.

Fig. 10. Two isomeric forms of a substituted ethylene. Two carbons joined by a double bond. Two isomers if at least two sorts of radicals are attached to the carbon: trans form (at left) with like radicals opposite; cis form (right) with like radicals adjacent.

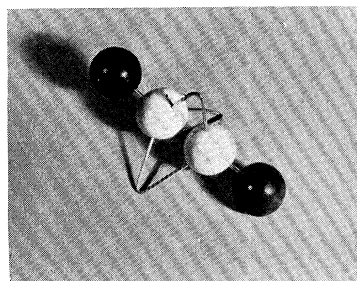


Fig. 11.

Fig. 11. C_2H_2 . A linear molecule with a triple bond.

An ordinary chain compound is shown in Fig. 12. The zig-zag structure of the compound, observed for example by Müller,⁵ is well shown in the figure.

The atoms beyond the tetravalent ones appear generally in ionic compounds rather than with valence bonds, and so do not concern us in this paper. But we should discuss one point: in a great many compounds there is ambiguity as to whether the bonds are homopolar or ionic. We have mentioned the silicates; other examples are $\text{H}-\text{Cl}$ (which could be written also H^+Cl^-) and $\text{H}-\text{O}-\text{H}$ (which could be written $\text{H}^+(\text{OH})^-$ or $\text{H}^+\text{O}=\text{H}^+$). Even such a compound as Al_2O_3 can be written in either way ($\text{Al}\begin{matrix} \diagup \text{O} \diagdown \\ \text{O} \\ \diagdown \text{O} \diagup \end{matrix}\text{Al}$ or $(\text{Al}^{+++})_2(\text{O}^-)_3$). Very general principles of wave mechanics tell us the outline of the treatment in these cases. The two explanations constitute two unperturbed states, from which the true one is to be found by linear combination, so that the real situation is intermediate between the two. If the energies of the two

⁴ E. Hückel, *Zeits. f. Physik* **60**, 423 (1930).

⁵ A. Müller, *Proc. Roy. Soc.* **A114**, 542 (1927).

models are approximately the same, the real state will lie roughly half way between, while if one has a much lower energy than the other, that will fairly accurately represent the real situation. Moreover, if the two are combined, there will be a resonance effect in the energy, which will generally bring the real energy lower than that computed from either model separately. This may well explain the unusual stability of the silicates, and of the other compounds we mentioned: their energy is lower on account of the two explanations of the binding.

It is important to consider the relation of our models, say for H_2O , to those of Debye,⁶ based on the assumption of ionic compounds in which the polarizability of the O^- is considered. Debye has been able to give alternative explanations even of the triangular form of H_2O and the pyramidal form of NH_3 . From the discussion of the last paragraphs, we see that both these explanations are to be regarded as legitimate starting points, with the true

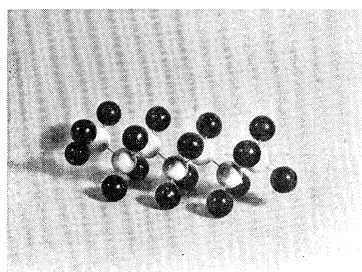


Fig. 12.

Fig. 12. A chain compound, C_7H_{16} . The zig-zag arrangement of carbons, and the elongated cross-section of the chain, result from having the valences of carbon inclined at definite angles to each other.

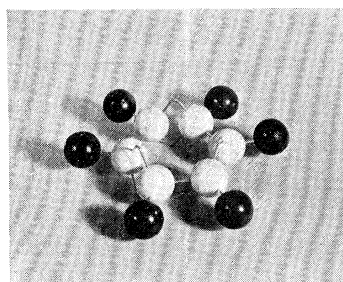


Fig. 13.

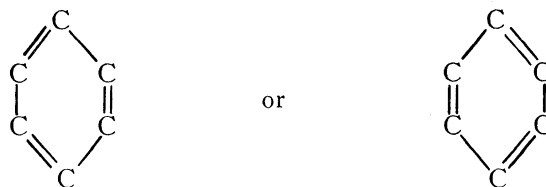
Fig. 13. Benzene, C_6H_6 . The Kekulé model.

state of affairs somewhere between them. The two descriptions, ionic and homopolar, are not as a matter of fact very different in fundamentals. Consider for example HCl . In the homopolar valence explanation, the electron from H , and one from Cl , are shared on the line joining the two atoms, and the net effect is that some of the hydrogen electron's charge has shifted toward the chlorine. In the ionic explanation, we start by assuming that the hydrogen electron is wholly transferred to the chlorine. But then we assume that polarization pulls some of it back again, and we are left in very much the same situation as before. The principal advantages of the homopolar method, with these ambiguous problems, are first that it seems rather nearer the real solution, as is shown, for example, by the small dipole moments of the hydrogen halides; and second that it is better able to deal in a general way with directional properties.

Another point connected with valence should be mentioned similar to the

⁶ P. Debye, "Polar Molecules," Chemical Catalog Co.

ambiguity between the ionic and homopolar valence descriptions of a compound. In some cases there may be several ways of drawing valence bonds in a given compound. In such cases, the real situation is again a combination of the various possibilities, and on account of resonance the energy is lower than it would otherwise be. We can not then draw the valence bonds in an unambiguous way; we must rather imagine them shared between several atoms. Such cases of shared valence may well be commoner than is usually supposed. The writer has already explained the cohesion in monovalent metals as coming from this effect, and it probably persists through most of the metals other than those specifically discussed in this page; for in all of these, each atom has more neighbors than it has electrons to share, and hence than it has valence bonds in the ordinary sense. Another example is probably found in the benzene ring. Here the Kekulé model, shown in Fig. 13, allows either the structure



By wave mechanics we should have a combination of these two possible structures, resulting in a complete equivalence of the carbons of the ring, a shared valence (essentially $1\frac{1}{2}$ bonds between each pair), and an added stability for the structure on account of the resonance effect on the energy. Still another case presumably comes in the existence of shared valences where ordinarily we suppose no valence at all to act. In H_2O , there is probably a little valence attraction between the two H's, just as if they were forming a H_2 molecule, and as a consequence the angle between the lines to the two H's should be slightly acute. And even between molecules we may expect this shared valence to act. In crystals like Te and Sb we have spoken as if all valence forces acted within the chains or plates of which the crystals are formed, but this undoubtedly is not the case. In complicated organic compounds, probably the valence forces between one molecule and another are nearly as strong as within a molecule. Substances where this is true will hang together to form solids, and it will be nearly as difficult to separate the molecules as to break up the individual molecules, so that an attempt to vaporize them by heating will be very likely to disrupt the whole structure instead, a common phenomenon with these complicated compounds. Many examples of polymerization may well be cases where valences formerly operative within a molecule have partly changed over to the role of intermolecular forces. It seems, then, that this phenomenon of shared valence is of common occurrence, and that an understanding of it, as well as of the relation between ionic and homopolar binding, is essential.

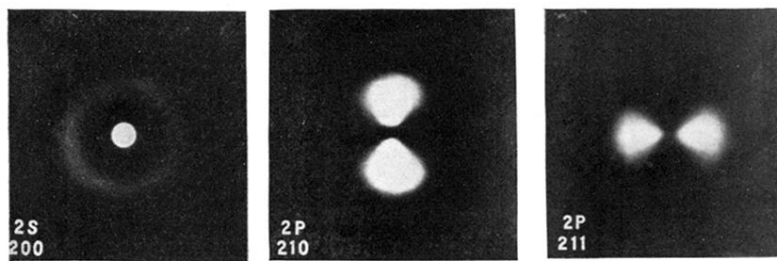


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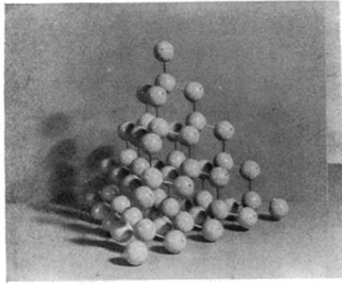


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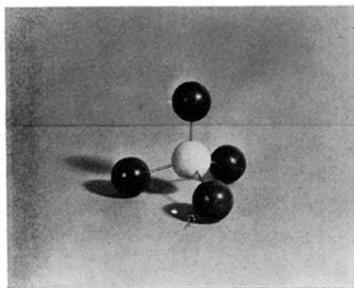


Fig. 9. CH₄.

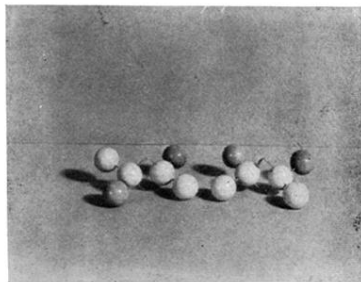


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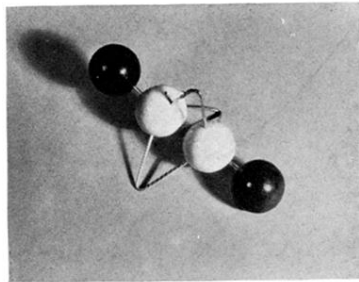


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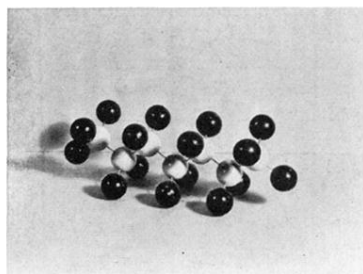


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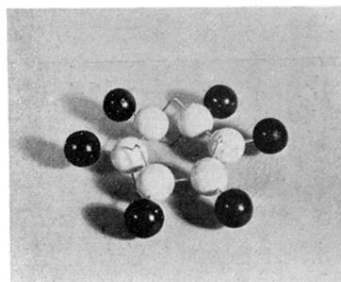


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Fig. 13. Benzene, C₆H₆. The Kekulé model.

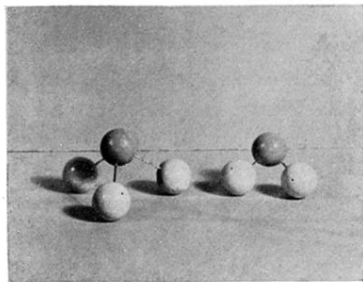


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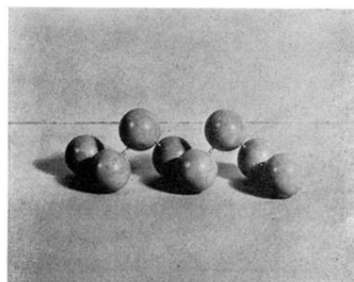


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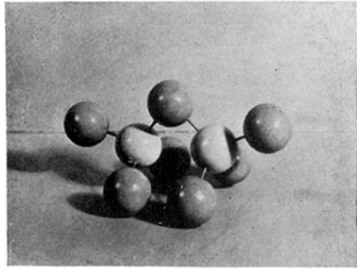


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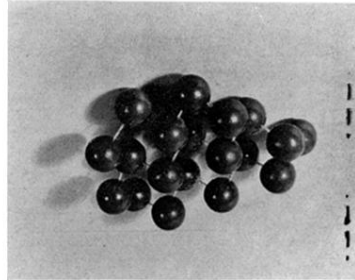


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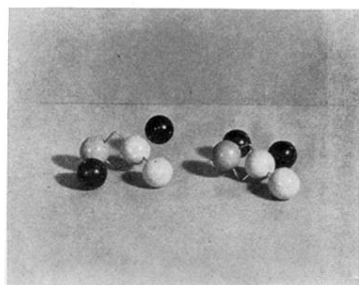


Fig. 6.

Fig. 6. Two isomeric forms of an oxime compound. A nitrogen and carbon are joined by a double bond. The two forms arise from the two possible orientations of the third valence of the nitrogen.

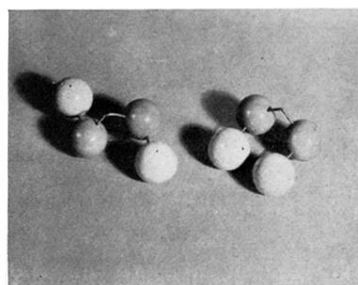


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