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The Theory of the Structure of Hydrogen Peroxide and Hydrazine

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The method of electron pairs has been applied to determine the most stable configuration for the atoms in the molecules $\text{HO}-\text{OH}$ and $\text{H}_2\text{N}-\text{NH}_2$. The calculations show that free rotation cannot occur in either of these molecules at ordinary temperatures and that the only stable forms are those in which the azimuth of one-half of the molecule with respect to the other is approximately 90° . The essential feature of the argument is that the

electrons of the two central atoms arrange themselves to form the strongest possible bonds and in so doing render the charge density on these atoms unsymmetrical about the axis of the molecule. The interaction of the two electronic clouds is the dominant factor in determining the azimuth of one group relative to the other; all other types of interaction have been estimated to shift the equilibrium position only slightly, i.e., probably from 90° to 100° .

INTRODUCTION

IN a contribution¹ to the recent Faraday Society discussion on dipole moments we proposed, for the hydrogen peroxide molecule HOOH and the hydrazine molecule H_2NNH_2 , forms which are highly unsymmetrical. We were led to our conclusions from a theoretical investigation of the electronic structures of these molecules, whence it appeared that the most important factor determining the azimuth of one-half of the molecule with respect to the other was the interaction of the two electronic clouds on the central atoms. It is the purpose of the present paper to describe the method of calculation rather than to discuss experimental facts which can be understood in the light of the final conclusions. The latter has been done already¹ and it was shown, for example, that the unsymmetrical forms of these molecules give a simple explanation of their large dipole moments and weak Raman spectra.

Two distinct methods have been developed for predicting the nuclear configuration of simple polyatomic molecules from a knowledge of the electronic configurations of the constituent atoms. These are known respectively as the method of electron pairs and the method of molecular orbitals and each has achieved a considerable measure of success. The strength of

the former method lies in the fact that the energy of the polyatomic molecule is obtained directly as a sum of exchange integrals, the coefficients of a few of which depend on the angle parameters determining the configuration of the molecule. Although the magnitudes of the exchange integrals are not known accurately, yet from the way in which the various angle parameters appear in the energy expression, it is often possible to decide which is the most stable configuration for the nuclei. On the other hand, the orbital method involves the solution of a secular determinant of very high order, in which the magnitudes of the resonance integrals are uncertain and the angle parameters appear on and off the diagonal. Unless this secular equation can actually be solved, either exactly or by some approximate method, to give the energy of the molecule as a linear combination of resonance integrals with coefficients depending on the angle parameters, one cannot in general determine the most stable configuration. The orbital method is best applied to the calculation of energy states when the arrangement of the atoms in the molecule is already known, because then symmetry properties usually ensure sufficient factorization of the secular equation to render it soluble. In what follows, we are interested only in the relative energies of various configurations, rather than in the exact evaluation of the energy states of one particular configuration, and shall therefore employ the method of electron pairs.

¹ W. G. Penney and G. B. B. M. Sutherland, Faraday Society Discussion on Dipole Moments, Oxford, 1934.

HYDROGEN PEROXIDE

The normal state of the oxygen atom is $(1s)^2(2s)^2(2p)^4\ ^3P$ but when the atom is in chemical combination with other atoms the L - S structure is partially destroyed. For accurate calculations on divalent oxygen one must therefore adopt wave functions which are linear combinations of those of $\ ^3P$, $\ ^1D$ and $\ ^1S$. It is a very good approximation with oxygen, but not with carbon or nitrogen, to neglect the presence in the wave function of states obtained from the ground configuration by promoting, for example, an electron from the $2s$ to the $2p$ shell. This is because the greater stability which the molecular bonds would thus acquire is not capable of supplying sufficient energy for the promotion.

The four $2p$ electrons of an oxygen atom in the divalent state can have only one reasonable disposition. Two are taken with the same orbital wave function but with opposite spins; the other two are taken with their axes of quantization perpendicular to each other and to that of the first pair. The latter two can then be considered as having their spins free and ready to form bonds with electrons on other atoms. Hence the L - S structure of the oxygen atom affects the energy of the H_2O_2 molecule in a way which depends very little on the angle parameters. Since we are interested solely in determining the best values of these parameters, we shall neglect the L - S forces altogether and base our calculations simply on $(2p)^4$.

For convenience we shall append a suffix a to any quantity relating to one of the OH groups and a suffix b to those of the other (Fig. 1).

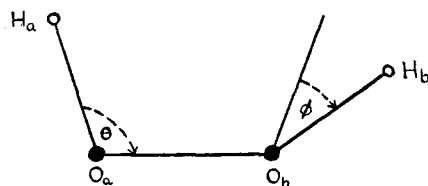


FIG. 1. The HOOH molecule.

Next, we take right-handed and left-handed sets of orthogonal axes (x, y, z) and (x', y', z') on O_a and O_b , respectively, with z and z' collinear but of opposite sense and with the xz plane containing H_a and the $x'z'$ plane containing H_b .

Let ϕ denote the angle between the x and x' axes and θ stand for either of the equal angles $H_aO_aO_b$ or $H_bO_bO_a$.

The choice of paired wave functions² is then as follows:

$$\left. \begin{aligned} \psi_a(2p\sigma_z), \quad \psi_b(2p\sigma_{z'}); \\ \psi_a(2p\sigma_x), \quad \psi_{H_a}(1s); \\ \psi_b(2p\sigma_{x'}), \quad \psi_{H_b}(1s); \\ \psi_a(2p\sigma_y), \quad \psi_a(2p\sigma_y); \\ \psi_b(2p\sigma_{y'}), \quad \psi_b(2p\sigma_{y'}). \end{aligned} \right\} \quad (1)$$

Here, for example, $\psi_a(2p\sigma_z)$ means a $2p$ wave function located on the O_a nucleus, with $m_l=0$ referred to the z axis of quantization, and has the form $zf(r)$.

For the evaluation of the energy we have the well-known expression

$$W = \sum_{i,k} Q_{ik} + \sum_i J_{ii} - \frac{1}{2} \sum_{\substack{i,k \\ i \neq k}} J_{ik} \quad (2)$$

in which the J_{ii} terms arise from the exchange energy between two electrons forming a bond, while those denoted by $-\frac{1}{2}J_{ik}$ come from the exchange energy between two electrons in different bonds. The terms Q_{ik} are the ordinary Coulomb forces between electron i on one atom and electron j on another. It is necessary to introduce two types of diatomic integral, those in which one electron is on an oxygen atom and the other on a hydrogen atom, and those where both electrons are on oxygen atoms. These integrals have been defined and discussed elsewhere³ but are repeated below for convenience.

$$\begin{aligned} Q_{\alpha\beta} &= \iint \psi_H(s_1) \psi_a(\alpha_2) H' \psi_H(s_1) \psi_a(\beta_2) dv_1 dv_2; \\ N_{\alpha\beta} &= - \iint \psi_a(\alpha_1) \psi_H(s_2) H' \psi_b(\beta_2) \psi_H(s_1) dv_1 dv_2 \\ Q_{\alpha\beta\gamma\delta} &= \iint \psi_a(\alpha_1) \psi_b(\beta_2) H' \psi_a(\gamma_1) \psi_b(\delta_2) dv_1 dv_2; \\ C_{\alpha\beta\gamma\delta} &= - \iint \psi_a(\alpha_1) \psi_b(\beta_2) H' \psi_b(\gamma_1) \psi_a(\delta_2) dv_1 dv_2. \end{aligned} \quad (3)$$

² We shall show later, when we come to consider the best value for θ , that some of the wave functions (1) have to be slightly modified in their directional properties. This correction may be disregarded for the present.

³ W. G. Penney, Proc. Roy. Soc. **A144**, 166 (1934).

Here H' is the usual diatomic perturbative potential for the two nuclei appearing in the integral.

Although it is not a difficult matter to write down the energy W given by (2) in terms of the integrals (3), we shall confine our attention for the moment to that part of W which depends on ϕ . Thus we neglect interaction between atoms not coupled by bonds and disregard the terms due to van der Waals and ionic forces. Then θ is clearly $\pi/2$ and W can be written

$$W = \text{Const.} + \frac{1}{2}(C_{\pi\pi\pi\pi} - C_{\pi\pi'\pi'\pi}) \cos^2 \phi + (D_{\pi\pi\pi\pi} - D_{\pi\pi'\pi'\pi}) \cos^2 \phi.$$

The value of $(C_{\pi\pi\pi\pi} - C_{\pi\pi'\pi'\pi})$ has been given as 1.5 e.v. by Pauling and Wheland⁴ and as 0.72 e.v. by one of the authors.⁵ The sign of $(D_{\pi\pi\pi\pi} - D_{\pi\pi'\pi'\pi})$ is certainly positive, and according to Bartlett and Furry⁶ is about equal in magnitude to $(C_{\pi\pi\pi\pi} - C_{\pi\pi'\pi'\pi})$. It is unfortunate that there is this uncertainty in the value of the coefficient of $\cos^2 \phi$ but it is surely safe to assume that the change in W as ϕ varies from $\pi/2$ to 0 or π is not less than half a volt and is most probably around one volt. It only remains to be shown that the above is the dominant factor in determining the shape of the molecule, and that the contributions from steric repulsions, ionic interactions and van der Waals forces in favor of more symmetrical dispositions of the atoms are not sufficient to alter appreciably the value $\phi = \pi/2$ or to permit of free rotation about the O—O axis.

The expression for the energy of H_2O_2 is a function of the angles θ and ϕ and if a value of θ is postulated then the value of ϕ which makes W a minimum clearly depends on the value of θ chosen. However, the energy is not equally sensitive to changes in these angles, being much more affected by changes in θ than by changes in ϕ . This follows since the energy of the OH bond depends strongly on θ , having its minimum at

$\theta = \pi/2$. To determine the values of θ and ϕ governing the most stable configuration we adopt a process of iteration, i.e., we choose a likely value of θ and, keeping it fixed, we determine the best value of ϕ . Then using this value for ϕ we try to verify whether our original assumption for θ is a good one.

Accordingly, let us for the moment make the rather naïve assumption that for all values of ϕ the net influence of H_b and O_b on H_a is the same as would be the steric repulsion on H_a of the other hydrogen atom in a water molecule containing H_a and O_a . The angle θ is then the angle of the water molecule, which evidence from several quarters⁷ has shown to be between 100° and 110° . We shall use for the present the value employed by Theilacker⁸ in his calculations on the electric moment of H_2O_2 , viz. $\theta = 110^\circ$. From the Morse function of Eyring and Polanyi⁹ we can now estimate the steric repulsion between H_a and H_b as a function of ϕ , provided we neglect the partial migration of the hydrogen electrons to the oxygen nuclei. Assuming that the O—O and O—H distances are 1.4Å and 1.0Å, respectively, we arrive at the following values for the variation of the H_a — H_b steric repulsion with ϕ (Table I). By taking a value of

TABLE I.

ϕ°	0	30	90	180
W e.v.	0.212	0.192	0.107	0.057

θ less than 110° it is found that these interactions become considerably larger, particularly near $\phi = 0$.

It might appear at first sight as though the interactions of H_a on O_b and of H_b on O_a would depend only on θ , but when one takes account of the fact that the density of electric charge around the oxygen atoms does not possess axial symmetry, it becomes evident that this interaction will also have a dependence on ϕ . The

⁴ L. Pauling and G. Wheland, J. Chem. Phys. **1**, 362 (1933).

⁵ W. G. Penney, Proc. Phys. Soc. London (1934).

⁶ J. H. Bartlett, Phys. Rev. **37**, 507 (1931); W. Furry and J. H. Bartlett, Phys. Rev. **38**, 1615 (1931). Actually $D_{\pi\pi\pi\pi}$ is about twice as large as $C_{\pi\pi\pi\pi}$ with $\alpha = \kappa R = 5$, and about equal at $\alpha = 6$. The equilibrium value α of the O—O distance in H_2O_2 is probably about 6.

⁷ R. Mecke *et al.*, Zeits. f. Physik **81**, 313, 445, 465 (1933); J. H. Van Vleck and P. C. Cross, J. Chem. Phys. **1**, 357 (1933).

⁸ W. Theilacker, Zeits. f. physik. Chemie **B20**, 142 (1933).

⁹ H. Eyring and M. Polanyi, Zeits. f. physik. Chemie **B12**, 279 (1933). We use, however, only 30 percent instead of 35 percent Morse function.

variation in W caused by this effect as ϕ changes from $\pi/2$ to 0 or π can readily be estimated from a table of integrals given by Ireland.¹⁰ By denoting the angle $\text{H}_a\text{O}_b\text{O}_a$ by α , the required variation in energy may be written in Ireland's notation as

$$\delta W = \sin^2 \alpha [2J_z(p^*p, bb) - 2J_{II}(p^*p, bb) - K_z(pb, p^*b) + K_{II}(pb, p^*b)],$$

where these integrals are to be evaluated at the H_aO_b distance. As shown later, the value of the effective internuclear distance R corresponding to this is very close to 5. At this value of R , the positions $\phi=0$ or π are only 0.04 e.v. more stable than the position $\phi=\pi/2$. This effect is therefore of minor importance.

Another type of interaction which contributes terms to the energy depending on ϕ is that arising from the mutual potential energy of the two OH dipoles. The evaluation of this effect by quantum mechanics is too difficult to be carried out here but it is easy to make a classical calculation which will give its approximate magnitude.¹¹ The dipole moment of the OH groups arises chiefly because some electronic charge migrates from its symmetrical position around the protons towards the oxygen nuclei. As an approximation we shall assume that the electric moment due to such a distortion of the electronic cloud may be represented by a point dipole situated two-thirds of the way along the OH line from the O atom and having its axis in the direction OH. Then applying the well-known formula for the mutual potential energy of two dipoles, we find that the variation of W with ϕ due to this effect is given by Table II. It is seen that the variation is not very large.

Summing up, we find that if θ is maintained at 110° , the variation of the energy with ϕ is

¹⁰ C. Ireland, Phys. Rev. **43**, 329 (1933).

¹¹ A molecule where the dipole interaction may be important is $(\text{CH}_2\text{OH})-(\text{CH}_2\text{Cl})$. The dipole moment of this molecule has been found to be independent of temperature over a wide range. Zahn (Faraday Society Discussion on Dipole Moments, Oxford, 1934) accounts for this by assuming that the H atom of the OH group resonates between being attached to O and to Cl, thus holding the O and the Cl together. It seems more natural to suppose that it is the interaction of the two ionic groups which prevents free rotation in this molecule.

TABLE II.

ϕ°	0	90	180
W e.v.	0.280	0.180	0.139

represented by a curve similar to that shown in Fig. 2. The potential energy is greatest at $\phi=0$ (or $\phi=2\pi$ of course) because here the $2p\pi-2p\pi$ interactions between the electrons of the oxygen atoms, the interaction between dipoles and between H atoms, are all large. Only the lack of axial symmetry of oxygen charge density favors this position, and this effect is small. The secondary maximum at $\phi=\pi$ arises because the $2p\pi-2p\pi$ interaction is partially compensated by the low values of the other types of interaction. The heights of the maxima are perhaps one volt and half a volt, respectively. The best value of ϕ would appear to be somewhere between 90° and 100° ; in our calculation¹ of the dipole moment of H_2O_2 we assumed the value 100° .

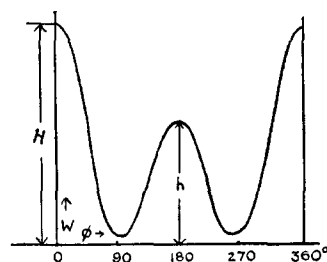


FIG. 2. The curve shows the variation in the energy of the HOOH molecule as the azimuth ϕ of one OH group to the other sweeps out the range $0 \leq \phi \leq 2\pi$. An exactly similar curve applies to the energy of the $\text{H}_2\text{N}-\text{NH}_2$ molecule. For HOOH the rough values of the maxima are $H=1.0$ e.v. and $h=0.5$ e.v., and for $\text{H}_2\text{N}-\text{NH}_2$, $H=0.33$ e.v. and $h=0.2$ e.v. The latter must be considered as more likely to be under- rather than overestimates.

The variation with θ

It is necessary now to investigate in greater detail the assumption that the best value of θ is 110° when ϕ is maintained at 90° , approximately its best value. To do this we consider separately the various terms in the energy depending on θ and find where their sum has its minimum. Before performing the calculations, however, we shall endeavor to explain the ideas underlying them. In the first place, if the

assumption of perfect pairing is made and all other interactions are neglected, θ has the value 90° . The repulsive interactions of O_b and H_b on H_a force H_a off the x -axis and thus increase θ . If the σ - σ bond between the oxygen atoms were infinitely strong, the disposition of the bonding electrons on the oxygen atoms would remain unaltered, one having its axis of quantization along z and the other along x . Actually, however, the axis of symmetry of the electron which is bonded to that of H_a will tilt a little from the x -axis, say through an angle ψ_2 , in order to preserve the O-H bonding energy as much as possible. Orthogonality conditions then require that the axis of symmetry of the other bonding electron of O_a also tilt through an angle ψ_2 , this time from the z -axis. If we denote by ψ_1 the angle between the line H_aO_a and the axis of quantization of the electron of O_a which is coupled to that of H_a , we have (Fig. 3)

$$\theta = \pi/2 + \psi_1 + \psi_2.$$

The relation between ψ_1 and ψ_2 is determined by the relative strengths of the O-H and O-O bonds.

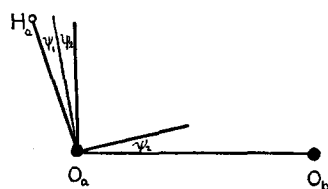


FIG. 3.

The dependence of W on ψ_1 and ψ_2 is given in the equation¹²

$$W = \text{Const.} + 3(N_{\pi\pi} - N_{\sigma\sigma}) \cos^2 \psi_1 - 3 \cos^4 \psi_2 C_{\sigma\sigma\sigma\sigma} / 2 + M(H_a, H_b) + 2M(H_a, O_b) + I(a, b). \quad (4)$$

In this expression the second and third terms correspond respectively to the energies of the O-H and O-O bonds, while $M(H_a, H_b)$ represents the steric repulsion of the two H atoms and $2M(H_a, O_b)$ the steric repulsion of H_a on O_b and H_b on O_a . Finally $I(a, b)$ gives the interaction between the two OH dipoles.

¹² We have neglected certain C integrals, the values of which are very small.

Next we investigate the relation between ψ_1 and ψ_2 . Since $C_{\sigma\sigma\sigma\sigma}$ is approximately equal to $(N_{\sigma\sigma} - N_{\pi\pi})$ and ψ_1 and ψ_2 are both small, (4) may be rewritten

$$W = \text{Const.} - 3A(1 - \psi_1^2) - 3A(1 - 2\psi_2^2)/2 + \dots,$$

and as $(\psi_1 + \psi_2)$ is fixed, this expression for W is clearly a minimum when $\psi_1 = \psi_2$. Hence

$$W = \text{Const.} + 6(N_{\sigma\sigma} - N_{\pi\pi})\psi^2 + M(H_a, H_b) + 2M(H_a, O_b) + I(a, b), \quad (5)$$

where $2\psi = \theta - \pi/2$. It now remains to evaluate the various terms in (5) and so find the value of θ for which W is a minimum.

The only term which offers any difficulty is $M(H_a, O_b)$ and the exact method by which it was obtained is described in the next paragraph. The function $M(H_a, H_b)$ was obtained simply from the Morse function of Eyring and Polanyi; the function $I(a, b)$ was obtained from the classical interaction of two dipoles; the value taken for $(N_{\sigma\sigma} - N_{\pi\pi})$ was 2.9 e.v.¹³ Fig. 4 shows

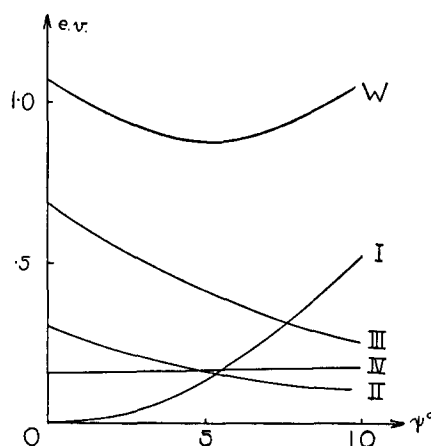


FIG. 4. The figure shows the variation in the energy W of the HOOH molecule with $\psi = (\theta - 90^\circ)/2$. The best value of θ is seen to be 100° . The constituent parts of W as given in Eq. (5) are shown as I, II, III and IV, respectively.

the variation of the separate terms with θ , and the upper curve shows W . It is seen that the best value of ψ is about 5° , corresponding to $\theta = 100^\circ$.

The function $M(H_a, O_b)$

The energy of an OH molecule in terms of Ireland's integrals, to the approximation of (2) is

¹³ J. H. Van Vleck, J. Chem. Phys. 2, 20 (1934).

$$W(\text{OH}) = 2J(ss, bb) + 3J_{\Pi}(p^*p, bb) + J_z(p^*p, bb) \\ - K(sb, sb) - 3K_{\Pi}(pb, p^*b)/2 + K_z(pb, p^*b).$$

Using the table of integrals given by Ireland, we find that this has its minimum at $R=2.63$. Now the O—H internuclear distance in the equilibrium position is known to be very nearly 1.0 Å and this gives us immediately the scale for R . Once again in terms of Ireland's integrals, the mutual energy of O_b and H_a in the position $\phi = \pi/2$ is

$$\delta W = [2J(ss, bb) + 3J_{\Pi}(p^*p, bb) + J_z(p^*p, bb) \\ - K(sb, sb) - 3K_{\Pi}(pb, p^*b)/2 \\ - K_z(pb, p^*b)/2] - \sin^2 \alpha [J_{\Pi}(p^*p, bb) \\ - J_z(p^*p, bb)] + \sin^2 \alpha [K_{\Pi}(pb, p^*b) \\ - K_z(pb, p^*b)]/2,$$

where α is the $H_a O_b O_a$ angle. The $O_a H_b$ distance in Angstroms is readily determined for various values of θ from the known O—O and O—H distances and the corresponding values of R are obtained from the scale factor already discussed. The variation of δW with θ is then found by using the table of integrals given by Ireland. As one would expect, the expression of δW is very sensitive to changes in the O—O distance. Fortunately, however, θ is rather insensitive to such a variation in δW so that on the whole our estimate of θ has a range of uncertainty of only a few degrees.

As a criticism of the above calculations, it might be urged that the numerical values employed for the integrals give far too low an energy of dissociation for the water molecule. Thus Coolidge¹⁴ finds from calculations similar in principle to those of Ireland, a theoretical value 3.5 e.v., assuming nonpolar wave functions, and 5.7 e.v. including polar terms, in contrast with the observed value 10 e.v. However, in our calculations on θ we are balancing various terms against each other and, as theoretical values are used throughout, it seems unlikely that our estimate $\theta = 100^\circ$ is far out.

HYDRAZINE

Calculations can be made on hydrazine very similar to those already described for hydrogen peroxide. The two additional hydrogen atoms complicate matters to some extent but the chief

difficulty arises from the fact that the $(2s)^2$ shell of the nitrogen atom shows a distinct tendency to break up under the influence of neighboring atoms. As a consequence, one has to deal not with a pure configuration $(2s)^2(2p)^3$ but with a mixture of $(2s)^2(2p)^3$ and $(2s)(2p)^4$. Although it is not possible to estimate the "coefficient of mixing" very accurately, yet its approximate value is readily perceived. As before, the L, S forces of the central atoms can be neglected since they have little to do with deciding the azimuth of one NH_2 group with respect to the other.

In a first attempt at constructing a model for the hydrazine molecule, one would naturally adopt for the three valencies of the nitrogen atom the three mutually orthogonal bonds of $(2p)^3$. Neglecting interactions between atoms not coupled by bonds, the molecule thus obtained would have the angles HNN , $H_1N_1H_2$, $H_2N_2H_4$, all 90° , and free rotation would occur about the N—N axis. However, when various types of steric repulsion are included, it is found that the interaction between the hydrogen atoms alone is sufficiently large to prevent free rotation at ordinary temperatures. In fact, the molecule is fixed quite firmly in the *trans* position, and in consequence this model has zero electric moment. The experimental observation¹⁵ that the dipole moment is quite large (1.83×10^{-18}) can only mean that there exists a more stable configuration than the one described.

Consider one of the $2s$ electrons extracted from a nitrogen atom; there remains a configuration $(2s)(2p)^3$, identical with that of the tetravalent carbon atom. Now it is well known that the four valencies of the carbon atom are disposed tetrahedrally, and that their great bonding power arises from the hybridization of the $2s$ and the $2p$ wave functions.¹⁶ If the $2s$ electron which was removed from the N atom is now restored, not into the $2s$ orbit but into one of the

¹⁵ L. F. Audrieth, W. Nespital and H. Ulich, J. Am. Chem. Soc. **55**, 673 (1933).

¹⁶ The hybridization of the s and p wave functions in the N atom was first discussed (with reference to the NH_3 molecule) by J. H. Van Vleck, J. Chem. Phys. **1**, 219 (1933). The importance of the hybridization has been further emphasized by W. G. Penney, Proc. Roy. Soc. (1934).

¹⁴ A. S. Coolidge, Phys. Rev. **42**, 189 (1932).

already singly-occupied tetrahedral orbitals, then an N atom is obtained with powerful valence bonds along three of the tetrahedral directions and with a pair of electrons of opposite spins occupying the fourth.¹⁷ A hydrazine molecule constructed from such nitrogen atoms is the most stable one possible (Fig. 5). An alternative

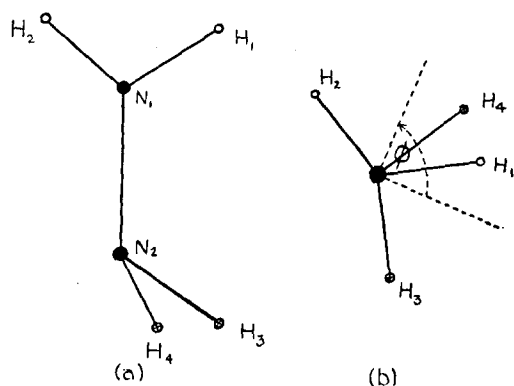


FIG. 5. Elevation (a) and plan (b) of the $\text{H}_2\text{N}-\text{NH}_2$ molecule.

way of picturing its formation is to imagine a hydrogen atom removed from each of two ammonia molecules and the two NH_2 residues coupled together along the line of their free valencies.

The tetrahedral wave functions can be written very simply as

$$\psi_t = \frac{1}{2}[\psi_N(2s) + (3)^{1/2}\psi_N(2p\sigma_t)],$$

where $\psi_N(2p\sigma_t)$ means a $2p$ wave function centered about the N atom with its axis of

¹⁷ We do not wish to imply that the bonds are exactly at the (regular) tetrahedral angle 109.5° , nor that the disposition of the bonds and the angle parameters of the model are unmodified by the various steric repulsions, ionic interactions and van der Waals forces. However, for our purpose these are small corrections and can be ignored.

quantization along the tetrahedral direction t . Using such wave functions and adopting the pairing of spins in the way discussed above, we find that the dependence of the energy W on the azimuth ϕ is given by

$$W = K + 4 \cos^2 \phi [(D_{\pi\pi\pi\pi} - D_{\pi\pi'\pi'\pi}) + \frac{1}{2}(C_{\pi\pi\pi\pi} - C_{\pi\pi'\pi'\pi})]/9. \quad (6)$$

Here K represents the effect of steric repulsions, ionic interactions and van der Waals forces and includes as well terms of the C and D types with coefficients depending on ϕ , but whose magnitude compared with that of $C_{\pi\pi\pi\pi}$ or $D_{\pi\pi\pi\pi}$ is negligible. Just as with HOOH it can readily be shown that the second term in (6) is the dominant factor in determining the relative orientation of the two NH_2 groups. There is no essential difference in the method employed, i.e., the various interactions (steric, ionic, etc.) are estimated for different values of ϕ , assuming $\theta = 110^\circ$. In performing the calculations we employed for the $\text{N}-\text{N}$ distance¹⁸ the value 1.5\AA and for the $\text{N}-\text{H}$ distance¹⁹ the value 1.02\AA . The final result is that the equilibrium position $\phi = 90^\circ$ given by the second term of (6) alone is perhaps modified to $\phi = 100^\circ$. Thus the curve illustrating the dependence of W on ϕ is similar to that of Fig. 2 with $H = \frac{1}{3}$ volt and $h = \frac{1}{3}$ volt.

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¹⁸ This was estimated from Badger's formula (J. Chem. Phys. **2**, 218 (1934)), by using 900 cm^{-1} as an approximate value of the frequency corresponding to the symmetrical oscillation of the two halves of the NH_2-NH_2 molecule. Compare data on the Raman spectra of N_2H_4 , Imanishi, Papers Inst. Tokyo **16**, 1 (1931); Sutherland, Nature **126**, 916 (1930).

¹⁹ This is taken from Dennison and Uhlenbeck's determination of the dimensions of the NH_3 molecule from infrared data, Phys. Rev. **41**, 313 (1932).