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of nonideal but also of ideal detonation. As a matter of fact, R_m/d values reproducibly greater than 4.0 have not been observed in any case in extensive studies of a number of ideal explosives in which density, particle size, and diameter were varied over wide ranges. While the observed wave shapes are not in agreement with the predictions of the curved front theory, it is clear from present results and numerous others that wave shape is dependent upon reaction rate and reaction zone length. In fact, from experimental evidence it does not seem

unlikely that all of the observed change in the R/d ratio may be associated with variations in the ratio a_0/d and that R_m/d would be about 3.0 to 4.0 in all cases in which $a_0 \ll d$, although it is not yet certain that a small density effect on R_m/d does not exist. Thus, the maximum observed value of R_m/d for low density fine-grained TNT was about 2.1, compared with 3.0 for high density (pressed) TNT of very small particle size, but the curve appears still to be increasing in the former at the maximum density studied.

Some Semiempirical Quantum-Mechanical Calculations for Ammonia and for Diimide

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Quantum-mechanical calculations by the naive, semiempirical LCAO MO method have been made for the ammonia and the diimide molecules. With the use of parameters obtained by fitting the empirical data for ammonia, it has been calculated that the activation energy for the syn-anti interconversion of diimide should be about 33 kcal per mole.

AS is now well known,¹ a trivalent nitrogen atom that forms three single bonds has normally a pyramidal configuration. It is, however, so easily distorted into a planar configuration that the isolation of the enantiomorphic forms of a tertiary amine, $NRR'R''$, has not yet been effected.¹ On the other hand, a trivalent nitrogen atom that forms one single and one double bond is able to maintain its preferred nonlinear configuration, so that the isolation of stereoisomeric oximes, azo compounds, etc. is ordinarily possible.¹ This paper is concerned with an attempt to provide a theoretical explanation for the striking difference between the configurational stabilities of the nitrogen atom in its different valence states.

The treatment is based on quantum-mechanical calculations of the activation energies for the inversion of ammonia, NH_3 , and for the interconversion of the syn and anti forms of the (actually unknown) diimide, $\text{HN}=\text{NH}$. With molecules as complicated as these, rigorous solutions of the wave equations are clearly quite impossible; and absolute, but still only approximate calculations of the type made recently by several authors² for a number of unsaturated hydrocarbons would be extremely tedious. We have accordingly adopted the naive, semiempirical LCAO MO (linear-combination-of-atomic-orbitals molecular-orbital) procedure; and, in order to derive values for the several

numerical parameters that are required, we have made use of the experimental data for ammonia.³

It will here be sufficient to describe in detail only the calculations for ammonia; those for diimide are so completely analogous that they require no special comment. The three hydrogen atoms of the former molecule are considered to lie in the xy -plane at the corners of an equilateral triangle, and with one hydrogen atom on the positive x -axis. The nitrogen atom lies on the positive z -axis. If the acute angle between the z -axis and each of the NH bonds is called θ , then the angle ϕ between any two NH bonds is given by the relation $\cos\phi = 1 - \frac{2}{3}\sin^2\theta$. When $\theta = 90^\circ$ and $\phi = 120^\circ$, the nitrogen atom is in the xy -plane, so that the molecule is planar. Experimentally,⁴ the molecule is most stable when $\theta \cong 68^\circ$, so that $\phi \cong 107^\circ$. For convenience in reference, the $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals of the nitrogen atom will be designated as s , x , y , and z , respectively, and the three hydrogen $1s$ orbitals will be designated as a , b , and c . The protons associated with these latter orbitals lie, respectively, at negative, positive, and zero values of y .

For the diagonal matrix elements of the energy, we shall use the letter α with suitable subscripts. Thus, $\alpha_{xx} = \int x H x d\tau$, $\alpha_{aa} = \int a H a d\tau$, and so on. Because of the symmetry of the molecule, $\alpha_{aa} = \alpha_{bb} = \alpha_{cc}$; the additional relation $\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$, although not rigorously required, must also be at least approximately correct and will hereafter be assumed.

¹ See any textbook of organic chemistry.

² See, for example, D. P. Craig, Proc. Roy. Soc. (London) **A202**, 498 (1950); R. S. Mulliken and R. G. Parr, J. Chem. Phys. **19**, 1271 (1951).

³ For an earlier theoretical treatment of the ammonia molecule, see M. A. Kovner, Compt. rend. acad. sci. U.R.S.S. **35**, 177 (1942) [Chem. Abstracts **37**, 1930 (1943)].

⁴ Cf. D. M. Dennison, Revs. Modern Phys. **12**, 175 (1940).

Two parameters, which must be evaluated empirically, have so far been introduced. One of these, $\alpha_{xx}-\alpha_{aa}$, is probably rather small in magnitude since the ionization potentials of a $2p$ electron on a nitrogen atom and of a $1s$ electron on a hydrogen atom are apparently not very different. According to Skinner and Pritchard,⁵ the energy required to remove a $2p$ electron from a nitrogen atom in its trivalent valence state is about 319 kcal per mole; on the other hand, that required to remove the $1s$ electron from a normal hydrogen atom is about 314 kcal per mole. This first parameter, $\alpha_{xx}-\alpha_{aa}$, will therefore be assumed to be equal to zero, so that we can set $\alpha_{xx}=\alpha_{aa}=\alpha$. The second parameter, $\alpha_{ss}-\alpha_{xx}=\alpha_{ss}-\alpha_{aa}=\alpha_{ss}-\alpha$, however, must be large in magnitude and negative in sign; its evaluation is discussed below.

For the nondiagonal matrix elements of the energy, we shall use the letter γ , again with suitable subscripts. Thus, $\gamma_{ax}=\int a\mathbf{H}xd\tau=\int x\mathbf{H}ad\tau$, $\gamma_{bs}=\int b\mathbf{H}s d\tau=\int s\mathbf{H}bd\tau$, and so on. Since, for any given pair of atomic orbitals i and j , the resonance integral γ_{ij} seems to be more or less proportional⁶ to the overlap integral $S_{ij}(=\int ijd\tau)$, we shall assume that $\gamma_{ij}=kS_{ij}$, where k

is an additional parameter that has the dimensions of energy and is negative in sign. The values of the various S_{ij} , with $i, j=a, b, c, s, x, y, z$, can be obtained from the tables of Mulliken, Rieke, Orloff, and Orloff.⁷

If the secular equation is now set up with respect to the following atomic orbitals or combinations of atomic orbitals

$$\begin{array}{ccc} (6)^{-\frac{1}{2}}(-a-b+2c) & (2)^{-\frac{1}{2}}(a-b) & (3)^{-\frac{1}{2}}(a+b+c), \\ x & y & s \\ & & z \end{array}$$

it automatically separates into two identical quadratic factors and one cubic factor. (If the molecule is planar, the cubic factor further separates into one quadratic and one linear factor.) This is, however, as far as the factorization can be carried on the basis of merely the symmetry of the system.

With the foregoing assumptions and approximations, and with also the further assumption that all the interactions between different hydrogen atoms can be ignored, the cubic factor of the secular equation (i.e., the factor arising from the three functions listed in the last of the above columns) can be shown to have the form

$$\begin{vmatrix} \alpha-w & (3)^{\frac{1}{2}}S_{as}(k-w) & (3)^{\frac{1}{2}}S_{cx}\cos\theta(k-w) \\ (3)^{\frac{1}{2}}S_{as}(k-w) & \alpha_{ss}-w & 0 \\ (3)^{\frac{1}{2}}S_{cx}\cos\theta(k-w) & 0 & \alpha-w \end{vmatrix}=0. \quad (1)$$

Here, w is the energy associated with the molecular orbital concerned, and all the remaining symbols have the meanings stated above. Two different procedures can now be adopted. On the one hand, we may assume that the overlap integrals between different atomic orbitals are negligibly small. Although this assumption is certainly incorrect and, in fact, is inconsistent with the above approximation of letting γ_{ij} be proportional to S_{ij} , it has been a characteristic feature of most LCAO MO treatments from the very beginning⁸ to the present time⁹; and, in several different semiempirical calculations¹⁰ of the type now under discussion, it has been found to introduce no significant error. On the other hand, we may adopt the theoretically better assumption that the overlap integrals are *not* negligibly small. In this way, as will be shown below, the calculations are made more complicated, but they are not changed in any fundamental way.

We shall first consider the simpler assumption that the overlap integrals, when they appear multiplied by w in the secular equation, can be set equal to zero. Since, however, we must retain the different assumption that

the resonance integrals are proportional to the *correct* values of the overlap integrals, the net effect of this simplification is merely to delete all the terms in w that appear off the main diagonal of the determinant. If the cubic factor that is given above in Eq. (1) is modified in this way, and if each of its elements is divided by the constant k , it is transformed into

$$\begin{vmatrix} x & (3)^{\frac{1}{2}}S_{as} & (3)^{\frac{1}{2}}S_{cx}\cos\theta \\ (3)^{\frac{1}{2}}S_{as} & x+\delta_s & 0 \\ (3)^{\frac{1}{2}}S_{cx}\cos\theta & 0 & x \end{vmatrix}=0, \quad (2)$$

where $x=(\alpha-w)/k$, so that $w=\alpha-kx$, and where $\alpha_{ss}=\alpha+\delta_s k$. Since, on integration, it is found⁷ that $S_{as}=S_{bs}=S_{cs}=0.541$ and $S_{cx}=0.402$, when the NH distance is 1.014 Å,⁴ this equation can now be solved by standard methods, and w can be obtained as a function of θ and of the parameters α , k , and δ_s . When all three (or four) factors of the secular equation have been treated in this way, seven different values of w are obtained. Since there are altogether eight electrons in the molecule (exclusive of those in the K -shell of the nitrogen atom, which are here ignored), two electrons must be assigned to each of the four most stable molecular orbitals. The total energy of the molecule, which is twice the sum of the four lowest values of w , then assumes the form

$$W=8\alpha+kf(\delta_s, \theta). \quad (3)$$

Since the function $f(\delta_s, \theta)$ is too complicated to be expressed explicitly in terms of its arguments δ_s and θ , the following procedure must be adopted. First, the depend-

⁵ H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.* **49**, 1254 (1953).

⁶ See p. 712 of R. S. Mulliken, *J. chim. phys.* **46**, 675 (1949).

⁷ Mulliken, Rieke, Orloff, and Orloff, *J. Chem. Phys.* **17**, 1248 (1949).

⁸ E. Hückel, *Z. Physik* **70**, 204 (1931).

⁹ For a recent study based on this approximation, see, for example, H. H. Jaffé, *J. Am. Chem. Soc.* **76**, 3527 (1954).

¹⁰ For one example among many, see G. W. Wheland, *J. Am. Chem. Soc.* **63**, 2025 (1941).

ence of W upon θ is calculated for a number of different values of the constant δ_s . In this way it is found by trial and error that, in order for W to reach a minimum value when $\theta \cong 68^\circ$, it is necessary that $\delta_s \cong 1.093$. With this value for δ_s , it is then found that $W(\theta = 90^\circ) - W(\theta = 68^\circ)$, the calculated activation energy for the inversion of ammonia, is approximately $-0.0232k$. Since the observed value of this quantity⁴ is about 6 kcal per mole, it follows that $k \cong -6/0.0232 = -259$ kcal per mole.

We shall wish later to consider in somewhat greater detail how satisfactory the present treatment really is for the description of the ammonia molecule, and we shall need also to make the corresponding calculations for the diimide molecule. First, however, let us outline the method for removing the above-mentioned inconsistency that arises from the simultaneous use of vanishing and nonvanishing values for the overlap integrals. Only a slight modification of the procedure that has previously been employed^{10,11} need here be made. It can be shown that, in the original cubic factor 1 of the secular equation, the energy w can never be equal to k ; consequently, each element of the determinant can be divided by $k-w$, rather than by k . (Since k is evaluated empirically in both this treatment and the preceding one, there is no reason for supposing that it must here, as above, be equal to about -259 kcal per mole.) As a result of this transformation, each of the nondiagonal terms in the determinant is brought into exactly the same form as in Eq. (2). The situation is different, however, with some of the diagonal terms, which accordingly require special treatment. The one in the middle of the determinant, for example, becomes

$$\frac{\alpha_{ss} - w}{k - w} = \frac{\alpha + \delta_s'(k - \alpha) - w}{k - w}, \quad (4)$$

where δ_s' is a new parameter defined by the relation $\alpha_{ss} = \alpha + \delta_s'(k - \alpha)$. Further modification of Eq. (4) leads successively to the result that

$$\begin{aligned} \frac{\alpha_{ss} - w}{k - w} &= \frac{\alpha - w - \delta_s'(\alpha - w) + \delta_s'(k - w)}{k - w} \\ &= \frac{\alpha - w}{k - w} (1 - \delta_s') + \delta_s' = y(1 - \delta_s') + \delta_s', \end{aligned}$$

where $y = (\alpha - w)/(k - w)$, so that $w = (\alpha - ky)/(1 - y)$. We now define the quantity x by the equation $x = y/(1 - y)$ and then, since $y = x/(1 + x)$,

$$w = \frac{\alpha - kx/(1 + x)}{1 - x/(1 + x)} = \alpha + \alpha x - kx = \alpha - x(k - \alpha). \quad (5)$$

When all the nondiagonal and diagonal elements of Eq. (1) are modified in the way described, this equation

becomes

$$\begin{vmatrix} y & (3)^1S_{as} & (3)^1S_{cz} \cos\theta \\ (3)^1S_{as} & (1 - \delta_s')y + \delta_s' & 0 \\ (3)^1S_{cz} \cos\theta & 0 & y \end{vmatrix} = 0.$$

Since the two remaining (quadratic) factors of the complete secular equation can be treated in exactly the same way, the energy of each molecular orbital can be expressed in the form 5. Consequently, the total energy of the molecule, which is again twice the sum of the energies of the four most stable molecular orbitals, can be written as

$$W = 8\alpha + (k - \alpha)f'(\delta_s', \theta).$$

(See Eq. (3).)

The procedure from this point is the same as that employed in the original treatment. Thus, it is found by trial and error that, in order for W to have a minimum when $\theta \cong 68^\circ$, it is necessary that $\delta_s' \cong 0.53$. The calculated value of $W(\theta = 90^\circ) - W(\theta = 68^\circ)$ is then approximately $-0.0110(k - \alpha)$, so that $k - \alpha \cong -6/0.0110 = -545$ kcal per mole.

We now turn to the question whether the foregoing treatments are in reasonably satisfactory agreement with the pertinent empirical data that were not explicitly used in the evaluation of the parameters δ_s , k , δ_s' , and $k - \alpha$. In the first place, we may note that the energy difference $\alpha_{ss} - \alpha$ is given by the first procedure as $\delta_s k = -1.093 \times 259 = -283$ kcal per mole, and by the second procedure as $\delta_s'(k - \alpha) \cong -0.53 \times 545 = -289$ kcal per mole. These two values not only are in excellent agreement with each other but also are of the correct order of magnitude. Skinner and Pritchard⁵ have estimated that the difference between the energies of the trivalent valence states of a nitrogen atom with the configurations $2s^2 2p^3$ and $2s 2p^4$ is about 301 kcal per mole.

A further check upon the reliability of the present calculations is afforded by a consideration of the way in which the total molecular energy W varies with the angle θ (or ϕ) over a fairly wide range of the latter variable. For this purpose, we may conveniently take as the "experimental" data the results which Manning¹² obtained by solving the vibrational wave equation for an ammonia molecule with a double-minimum potential function. As is shown in Table I, the agreement of the calculated values with each other and with the "observed" ones are at least as good as could have been hoped for. Indeed, over the range $65^\circ \leq \theta \leq 90^\circ$ (or $103^\circ 25' \leq \phi \leq 120^\circ$) the first treatment, in which overlap is ignored, gives results that are almost identical with Manning's. For smaller values of θ (or ϕ), the agreement is somewhat poorer, but it is doubtless quite satisfactory at all angles that are either theoretically or experimentally significant. As is perhaps not entirely unexpected, the second, more refined treatment, in which overlap is taken explicitly into account, is apparently a

¹¹ G. W. Wheland, J. Am. Chem. Soc. 64, 900 (1942).

¹² M. F. Manning, J. Chem. Phys. 3, 136 (1935).

TABLE I. Calculated and "observed" values of the energy of ammonia.

| θ | ϕ | I ^b | W ^a II ^c | III ^d |
|----------|----------|----------------|-----------------------------------|------------------|
| 90° | 120° | 0.00 | 0.00 | 0.00 |
| 88° | 119° 51' | -0.12 | ... | -0.12 |
| 85° | 119° 15' | -0.70 | -0.59 | -0.71 |
| 80° | 117° 3' | -2.48 | -2.31 | -2.39 |
| 75° | 113° 33' | -4.54 | -4.38 | -4.65 |
| 70° | 108° 56' | -5.88 | -5.86 | -5.91 |
| 69° | 107° 54' | -5.98 | -5.98 | -5.99 |
| 68° | 106° 50' | -6.00 | -6.00 | -6.00 |
| 67° | 105° 44' | -5.96 | -5.97 | -5.93 |
| 65° | 103° 25' | -5.58 | -5.13 | -5.56 |
| 60° | 97° 11' | -2.88 | -2.32 | -3.31 |
| 55° | 90° 22' | 2.77 | 7.69 | 0.74 |
| 45° | 75° 31' | 22.25 | 33.14 | 12.33 |
| 30° | 51° 17' | 95.02 | ... | 32.05 |

^a W is the total energy of the ammonia molecule, in kcal per mole, expressed with respect to the energy of the planar configuration.

^b Calculated with neglect of overlap.

^c Calculated with inclusion of overlap.

^d The values in this column are those of Manning. See reference 12.

little less reliable than the original, cruder one; the difference, however, is not great. The errors, if indeed they are errors, may be due to the assumption that α_{aa} and α_{zz} can be assigned the same value α , or to the neglect of the hydrogen-hydrogen interactions, but we shall here make no attempt to explore either of these possibilities.

Since, in the treatment of the ammonia molecule, the explicit inclusion of the overlap integrals not only somewhat complicates the calculations but also slightly decreases the reliability of the results obtained, we shall here ignore these integrals in our treatment of diimide. The procedure has already been described and so now needs no further comment. We may, however, note that there are no additional numerical parameters that must be considered, since the only ones that enter are the same δ , and k which we have already evaluated. Consequently, the most stable shape of the diimide molecule and the activation energy for the syn-anti interconversion can be directly computed.

With the assumptions that the NH distance is again 1.014 Å, that the NN distance is 1.23 Å, and that all the overlap integrals have the values derivable from the table of Mulliken, Rieke, Orloff, and Orloff,⁷ the most stable NNH angle is calculated to be about 100°. To the present approximation of neglecting the hydrogen-

hydrogen interactions, the syn and anti forms of course have the same energy. The completely linear molecule, however, is approximately 106 kcal per mole less stable than the bent one. If the syn-anti interconversion is presumed to go through a planar intermediate in which one NNH angle is 180° whereas the other is allowed to take on whatever value leads to the most stable configuration, the calculated activation energy becomes about 33 kcal per mole for an activated complex in which the NNH angle that is *not* equal to 180° has the surprisingly low value of 76°. The alternative *nonplanar* activated complex, which would be involved if the reaction proceeded by a rotation about the nitrogen-nitrogen bond, was not considered; such an intermediate would require rupture of the pi component of the double bond, and so ought to be relatively unstable.

There is, unfortunately, no way in which the conclusions regarding the diimide molecule, which were stated in the preceding paragraph, can be compared with experiment. Diimide itself is unknown, and its closest analog for which data are available is azobenzene. With this aromatic molecule, the NNC angle is 121°–123°,¹³ and the activation energy for the transition syn→anti is about 23 kcal per mole.¹⁴ The differences between these experimental values and the corresponding ones calculated for diimide are no greater, however, than could reasonably be attributed to the considerable difference between the structures of the molecules that are being compared. In particular, it is of interest that the activation energy for the *cis-trans* interconversion about a *carbon-carbon* double bond, which has a value of perhaps 65 kcal per mole in 1,2-dideuteroethylene,¹⁵ is decreased to only 43 kcal per mole in stilbene.¹⁶ The most significant result of the calculations is therefore the purely qualitative one that, in agreement with experiment, a trivalent nitrogen atom that forms one double and one single bond should be much better able to maintain its stereochemical configuration than is one that forms three single bonds.

¹³ G. C. Hampson and J. M. Robertson, *J. Chem. Soc.* **1941**, 409; de Lange, Robertson, and Woodward, *Proc. Roy. Soc. (London)* **A171**, 398 (1939).

¹⁴ G. S. Hartley, *J. Chem. Soc.* **1938**, 633; Halpern, Brady, and Winkler, *Can. J. Research* **B28**, 140 (1950).

¹⁵ Douglas, Rabinovitch, and Looney, *J. Chem. Phys.* **23**, 315 (1955).

¹⁶ G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.* **56**, 638 (1934).