VALENCE BONDING IN NITROGEN COMPOUNDS

W. J. ORVILLE-THOMAS

The Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, Wales

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I. INTRODUCTION

The valence states of carbon and the variations in its bonding are primary considerations in the determination of organic molecular structures; these aspects are frequently reviewed and the refinement of observational data and theoretical concepts are regularly discussed. In the variety and interest of its valence states nitrogen stands second only to carbon, and the relations arising in its case are both significant in themselves and of importance in the wide variety of nitrogen-containing organic and biologically active molecules. The standard account of nitrogen structures is, of course, the Sidgwick volume, *The Organic Chemistry of Nitrogen*, revised by Wilson Baker and T. W. J. Taylor. This edition was published in 1947, and since that date a considerable body of more precise data on simple structures and of knowledge in relation to valence principles has become available.

In this review an attempt is made to classify the types of chemical bonding exhibited by nitrogen. The examples chosen are, deliberately, the simpler ones of their class. It will be seen that the variety and flexibility in the valence states of nitrogen make it, structurally, an element of exceptional interest.

Atoms in a molecule are joined together by electronic binding, and in order to describe a chemical bond it is necessary to obtain information concerning the electronic distribution in it.

The proper interpretation of experimental data such as bond lengths, bond energies, vibrational frequencies, dipole moments, and derived quantities such as bond orders and force constants yields a great deal of information about the intimate electronic structure of valence bonds.

Standard values for these quantities can be chosen for bonds to nitrogen which are essentially single, double, or triple in character. Experimentally derived data can then be compared with these "standard" values and deductions drawn as to the nature of the valence bonding. If the molecular parameters in a molecule differ significantly from these normal "standard" values, then this may be taken as an indication that bonds of a hybrid character are present. These receive a ready explanation in terms of delocalized π-type molecular orbitals.

On this experimental basis information may be obtained concerning the multiplicity and degree of ionic character of chemical bonds. We are then faced with the problem of interpreting this information in terms of the electronic structure of the molecules, i.e., in terms of valence theory. There are two chief approaches to the theory of molecular electronic structures, known respectively as the valence-bond and the molecular orbital theories. Both methods depend upon various approximations and neither is completely satisfactory. It is encouraging to find, however, that in most of their conclusions the two theories agree; they are best looked upon as being complementary and not as rival theories. In most cases a deeper understanding is obtained by a comparison of the two interpretations of chemical binding.

In this review advantage has been taken of the approximate physical picture of the electron distribution provided by the molecular orbital approach. It may be emphasized that the simple representation so provided is at best a first approximation to the actual electron-density distribution.

II. CHARACTERISTICS OF BONDS

A. Bond lengths and bond orders

In considering the effective covalent radius of an atom due regard must be given to the bond order of the linkage being studied, since atomic radii depend upon the valence state of the atom. Empirical equations connecting bond length with factors such as electronegativity have been put forward by Schomaker and Stevenson (80) and Gordy (31). The values currently accepted for pure single, double, and triple bonds to nitrogen are given in table 1.

Quantum-mechanical calculations in general predict the bond orders of the various links in a molecule. Sufficient experimental and theoretical data now exist

TABLE 1

Bond lengths for NX *links*

Link	NC	NN	NO	NS	Bond order
Single-bond length	1.47	1.47	1.43	1.69	1
Double-bond length	1.27	1.25	1.16	1.49	2
Triple-bond length	1.16	1.10	—	—	3

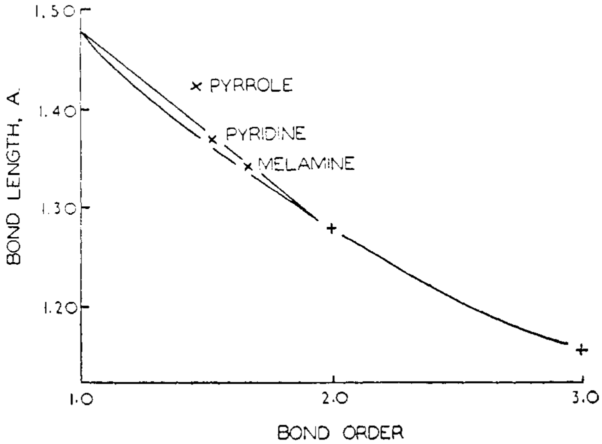


Fig. 1. Bond order/bond length curves for carbon–nitrogen links (Cox and Jeffrey (17)) Reproduced by permission of the Royal Society.

to enable bond order/bond length curves to be drawn for certain atom pairs (2, 17) (see figure 1). These curves yield valuable information as to the valence bonding in those cases where experimental bond lengths are known but the theoretical bond-order calculations have not been carried out. The bond-order values thus derived indicate which of the allowed molecular orbitals are filled, leading to a more complete physical picture of the chemical bonding.

These bond order/bond length curves, where they exist in a sufficiently exact form, may be used to give more precise information than is obtained by comparing the experimentally or empirically determined bond length with the standard single-bond, double-bond, or triple-bond values.

For those atom pairs where reliable bond length/bond order curves have not been obtained, the order of the bond may be estimated from its length by means of such empirical relations as the one proposed by Gordy (32). This has the form:

$$N = a/r^2 + b$$

a and b are constants depending upon the pair of atoms forming the bond. This relation can be put in the form:

$$N = \frac{r^{-2} - r_2^{-2}}{r_2^{-2} - r_1^{-2}} + 2$$

TABLE 2

Characteristic bond-stretching frequencies and force constants of NX bonds

Group	Bond-stretching Frequency	Force Constant	Group	Bond-stretching Frequency	Force Constant
	cm.$^{-1}$	*10*^{5} *dynes/cm.*		*cm.*$^{-1}$	*10*^{5} *dynes/cm.*
C—N..............	1050	5.5	N═N............	1600	—
C═N..............	1700	—	N—O............	1000	—
C≡N..............	2250	17.7	N═O............	1700	—
N≡C..............	2100–2200	16.3	NH..............	3100–3500	~6.0
N—N..............	825	—			

where r is the bond length observed, and r_1 and r_2 are the normal single-bond and double-bond lengths, respectively.

B. Bond angles

Changes in hybridization at the central atom have a pronounced effect upon interbond angles. s orbitals have no directional properties; when pure p orbitals are used for bonding the bonds are at right angles to each other; bonds formed from sp^3 orbitals make angles of 109°28′ with each other; complete sp^2 and sp hybridization leads to bond angles of 120° and 180°. For these three basic s, p hybridizations the hybrid atomic orbitals are equivalent. All intermediate degrees of hybridization can occur, but not all the resulting orbitals will be equivalent.

When the experimental data on molecular structure are examined it is found that the interbond angles do not always possess the "ideal" values quoted above for hybrid orbitals. These variations are due to the interactions between nonbonded atoms, to bond/bond interactions, and to lone-pair orbital/bond repulsions. To some extent the state of hybridization of the central atom can change from the "ideal" value to one more nearly corresponding with the molecular parameters as measured experimentally. As a general rule, when deviations from the "ideal" angles are found, part of the deviation can be explained by a hybridization change at the central atom.

C. Vibrational frequencies and force constants

Empirical correlations connecting the appearance of characteristic frequencies in vibrational spectra with the presence of certain groupings within a molecule lead to considerable information as to its structure. Vibration frequencies characteristic of NX bonds are given in table 2.

Recently correlations of bond lengths with stretching frequencies for carbon–nitrogen, nitrogen–nitrogen, and nitrogen–oxygen bonds have been presented (45, 48) (figures 2, 3, and 4). These curves are valuable in obtaining estimates of bond lengths in those cases where the bond-stretching frequencies have been assigned. An estimate of the bond order for these links can then be obtained from the length.

Force constants provide a quantitative measure of the forces involved in chemical bonding. It is to be expected that when the bond-stretching force con-

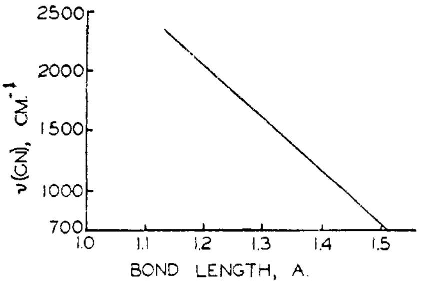


FIG. 2

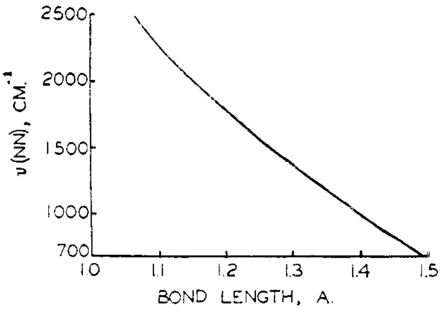


FIG. 3

FIG. 2. Relation between CN stretching frequency and bond length (Lüttke (49))
FIG. 3. Relation between NN stretching frequency and bond length (Lüttke (49))

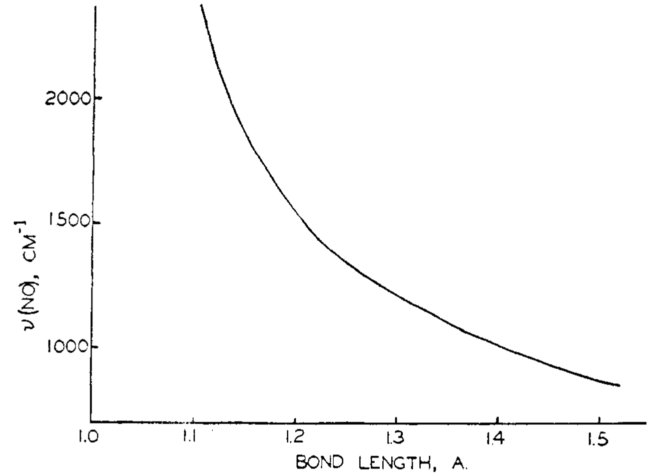


FIG. 4. Relation between NO stretching frequency and bond length (Lüttke (48))

stants between an atom pair in different molecules have similar values, then the electronic structure of the chemical bonds joining the atom pairs will be similar. The force constant for a particular bond remains reasonably constant, however, only if the environment of the bond in the different molecules does not vary markedly. Variation in the values of force constants can then provide information concerning changes in hybridization of an atom as we go from one molecule to another. The values for force constants associated with "normal" single, double, and triple bonds to nitrogen are given in table 2.

In those cases where reliable bond-stretching force constants have been calculated the bond orders may be obtained from an empirical relation proposed by Gordy (30) connecting bond order and bond length with force constant, f:

$$f = 1.67N\left(\frac{X_A X_B}{r^2}\right)^{3/4} + 0.30$$

X_A and X_B are the electronegativities of the atoms A and B forming the bond whose length is r.

D. Nuclear quadrupole coupling constants

Recently the interpretation of nuclear quadrupole coupling constants has led to information on the electronic structure of molecules (64). In some cases coupling constants give direct information on the valence states of atoms in molecules. When nitrogen is triply bonded, as in NH_3 and in the XCN series, the N^{14} coupling constant is about -4 Mc. per second. The molecules CH_3NC and NNO possess quadrivalent nitrogen atoms whose coupling constants are found to be very small, since the surrounding valence-shell electrons are nearly spherically distributed.

In this manner coupling constants afford a new and powerful source of information about chemical bonds.

III. MOLECULAR ORBITAL DESCRIPTION OF CHEMICAL BONDS

Nitrogen, which has five valence electrons, has two normal valence states: (*1*) trivalent, as in ammonia, six electrons of the valence group of eight being shared, and (*2*) quadrivalent with a completely shared octet.

Classical structural valence theory has proved inadequate to explain the structure of certain molecules containing nitrogen; nitrous oxide and hydrazoic acid, for instance, were considered to contain a quinquevalent nitrogen atom and were given the classical structures $O{=}N{\equiv}N$ and $H{-}N{=}N{\equiv}N$. Samuel endeavored to produce some support for a 5-covalent nitrogen atom (74–79). His views were criticized by Wheland (92), using valence-bond theory.

There is no satisfactory evidence for the 5-covalent nitrogen atom postulated by Samuel. On the basis of force constant data and the derived bond orders it has been shown that the central nitrogen atoms in nitrous oxide (NNO) and in hydrazoic acid (HNNN) are quadrivalent (60–62). In all molecules where the classical structure indicates a quinquevalent nitrogen atom the molecular orbital method indicates unequivocally a quadrivalent nitrogen atom.

In his series of papers Samuel criticized the use of the concept of a coördinate link and pointed out that there was no justification for assuming the existence of a second type of covalent link. This criticism seems justified, and in the subsequent discussion of the electronic binding in compounds containing 4-covalent nitrogen it will be seen that when the language of molecular orbital theory is used, the necessity for a second different type of covalent linkage disappears. This, of course, arises from the impossibility of knowing the origin of the electrons which are fed into the molecular orbitals concerned. These orbitals are an expression of the electron distribution in the molecule and so a function of its whole structure.

The molecular orbital theory supposes that each electron in a molecule is described by a wave function, ψ. This wave function represents the orbit of the electron in the molecule and is consequently called a molecular orbital. Each wave function has a definite energy value associated with it. The total energy for the molecule is, to a first approximation, the sum of the energies of the occupied molecular orbitals.

The quantity $|\psi|^2$ gives a measure of the density of the charge cloud associated with the molecular orbital. The orbital may be represented diagrammatically by drawing a boundary surface which effectively delineates the contour of the charge cloud.

Each molecular orbital may be built up by means of a linear combination of appropriate atomic orbitals (54, 56). In describing a molecule it is necessary to determine the allowed molecular orbitals and then follow the "aufbau" process in which the available electrons are fed into these molecular orbitals (in order of decreasing binding energy), due account being taken of the Pauli exclusion principle.

The molecular orbitals in many polyatomic molecules can be regarded as being localized between two atoms, e.g., in ammonia the following three localized molecular orbitals, each accommodating two electrons, lead to the formation of σ bonds. They are formed by the maximum overlapping of the constituent atomic orbitals.

$$\psi_1 = \phi(\mathrm{H}'\!:\!1s) + \phi(\mathrm{N}\!:\!2p_x)$$

$$\psi_2 = \phi(\mathrm{H}''\!:\!1s) + \phi(\mathrm{N}\!:\!2p_y)$$

$$\psi_3 = \phi(\mathrm{H}'''\!:\!1s) + \phi(\mathrm{N}\!:\!2p_z)$$

This concept of localized molecular orbitals forms the basis of an electronic theory of stereochemistry. In ammonia if pure $2p$ atomic orbitals of nitrogen were used in conjunction with the $1s$ atomic orbitals of hydrogen to form molecular orbitals, then the σ bonds arising from the feeding in of electrons to these molecular orbitals would make angles of 90° with each other.

A different type of molecular orbital can be formed by the overlap of two parallel atomic p orbitals belonging to adjacent atoms. The feeding in of two electrons of opposite spin into this type of molecular orbital leads to the formation of a localized π bond (figure 5). The molecular orbital has the form

$$\psi = l\phi(\mathrm{N}\!:\!2p_y) + m\phi(\mathrm{X}\!:\!np_y) \tag{1}$$

and a localized π bond, π_L, is formed if two electrons of opposite spin are fed into the orbital.

In certain molecules, however, the concept of localized molecular orbitals breaks down completely and π-type molecular orbitals delocalized over three or

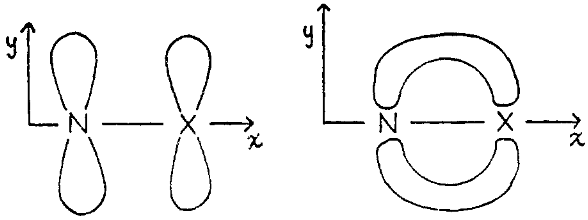


FIG. 5. Formation of a localized π bond

more nuclei are postulated as being present. The wave function of a π electron may be expressed as a linear combination of atomic orbitals (L.C.A.O.):

$$\psi = a_1\phi_1 + a_2\phi_2 + \dots + a_k\phi_k$$

The normalized coefficients, a_k, provide a measure of the relative time the electron spends in the vicinity of the different atoms 1, 2, ... k. Coulson (13) has given the following expression for the total bond order, N, of a bond r—s:

$$N = 1 + \Sigma a_r^{(n)} a_s^{(n)}$$

The summation extends over all n π electrons; the unit value represents the contribution of the σ bond.

In molecules such as benzene the approximation of considering σ bonds and π bonds as being entirely separate is most useful for the physical visualization of the valence bonds. The σ bonds are considered to be entirely localized, while the electrons in the π bonds are delocalized. Such delocalized electrons are known as mobile electrons.

In order to determine to what extent π and σ electrons are distinct from one another, Coulson, March, and Altmann (16) have made extensive calculations of the charge cloud in benzene. Their results are most interesting and indicate that the charge cloud has a considerable density *in the center of the ring.* Most significant of all, however, is their conclusion that there is only a small region, immediately above the six carbon nuclei, where the contribution of the π electrons is as great as that of the σ electrons. In effect the π electrons seem to be submerged in a larger cloud of σ electrons; i.e., the double streamers of the π cloud do not lie outside, or separate from, the σ cloud. It is apparent, then, that when σ and π electrons are dealt with separately, the physical picture obtained is inevitably approximate in nature.

Hybridization

The bonds formed between atoms will be such that the energy of the molecule will be a minimum. With this condition the bonds will have maximum strength. It has been found that stronger bonds can be formed by the combination of hybridized atomic orbitals than are possible by the use of pure s, p, etc. atomic orbitals. The concept of hybridized atomic orbitals is essential for the understanding of the detailed stereochemistry of molecules.

Experimentally it has been shown that the $\angle$ HNH in ammonia has a value near 109°. This indicates that the bonding atomic orbitals of nitrogen are not pure $2p$. The angle has very nearly the tetrahedral value and, to provide maximum overlap with the $1s$ orbitals of hydrogen, it follows that the atomic orbitals of nitrogen are very nearly sp^3 hybridized and that the lone-pair orbital will also be tetrahedrally disposed.

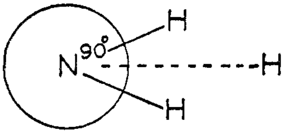
The hybridized atomic orbitals are markedly directional in character and provide greater overlapping in the σ bond, leading to the formation of stronger bonds. When the valence electrons of an atom have been placed in hybridized atomic orbitals which are to combine with other atomic orbitals to form molecular orbitals, we say that the atom is in its valence state. Isolated atoms do not normally exist in the valence state. The usefulness of this hypothetical state lies in the ease with which it enables the formation of molecules to be pictured. In ammonia the valence state of the nitrogen atom may be expressed symbolically as

$$\mathrm{N}[(1s)^2(2s + \delta 2p)^2(2p + \delta 2s)^3]$$

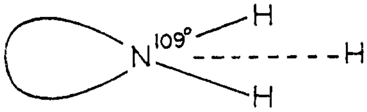
The symbol $\mathrm{N}(2s + \delta 2p)$ stands for a hybridized orbital formed by the $2s$ orbital of nitrogen acquiring some $2p$ character. This simple representation has no quantitative significance. In ammonia the HNH angles indicate that the σ-bond-forming atomic orbitals of nitrogen and the lone-pair orbital possess about 25 per cent s character.

As a result of the hybridization of the nitrogen atom the nitrogen lone-pair electrons, originally $2s^2$ in configuration, are in an orbital which possesses some p character. The boundary surface of this molecular orbital will project perpendicularly to the plane of the hydrogen atoms. This hybridized lone-pair non-bonding orbital forms an atomic dipole, which contributes substantially to the total dipole moment of the molecule.

The following diagrams show the ammonia molecule with the lone-pair electrons in a pure $2s$ orbital in (a) and in a hybridized orbital in (b). In (a) the center of negative charge in the lone-pair orbital is at the nitrogen nucleus; this is not so in (b) and an atomic dipole exists in the molecule.



(a)



(b)

The degree of hybridization occurring depends upon the molecular environment of the atom under consideration. When the atoms attached to the central atom are dissimilar, the hybridized atomic orbitals of this atom need not be identical and it is found that all intermediate degrees of hybridization can occur. The only necessary condition is that the hybrid atomic orbitals be orthogonal.

Coulson (14) in a study of carbon–hydrogen bonds has shown that bond lengths depend on the state of hybridization of the orbitals forming the bond. The experimental data indicate that the length of a bond to carbon decreases as the s character of the carbon orbital increases. The decrease in the covalent radius of carbon is 0.02 A. in passing from sp^3 hybrid orbitals to sp^2 hybrids, and 0.02 A. in passing from sp^2 hybrid to sp hybrid orbitals. Similar changes are to be expected for bonds to nitrogen. In addition it is now fairly clear that the state of hybridization of atoms changes during vibration (46, 50) and rotation (18, 65).

IV. VALENCE STATES OF THE NITROGEN ATOM

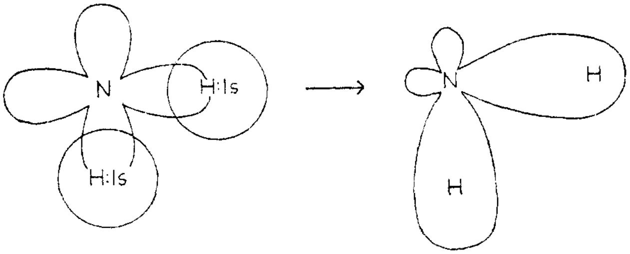
Walsh (89) in a notable series of papers has listed the orbitals possible for molecules of various configurations. His results, obtained in general terms, can be adapted to describe the bonding in nitrogen compounds.

The nitrogen atom in varying molecular environments can have associated with it a number of different combinations of σ bonds, localized π bonds (π_L), and delocalized π bonds (π_D). These bonds may be pictured as being produced by feeding electrons into molecular orbitals formed by the combination of the atomic orbitals of the combining atoms.

V. DIVALENT NITROGEN

Nitrogen is divalent in the NH_2^- ion and in the NH_2 radical. The lowest-energy molecular orbitals of an NH_2 system which can be built from pure *s* and *p* atomic orbitals only are:

(i) Two σ-type orbitals binding the hydrogen atoms to the central nitrogen atom. These orbitals are formed by the overlap of a 2*p* atomic orbital of nitrogen with the 1*s* atomic orbital of hydrogen. They are predominantly localized, one in each nitrogen–hydrogen bond.



The wave function for the molecular orbital is of the form

$$\psi = a\phi(\text{N}:2p) + b\phi(\text{H}:1s)$$

The polarity of the bond will depend on the relative values of the coefficients *a* and *b*.

(ii) A *p* orbital on the nitrogen atom pointing at right angles to the HNH plane.

(iii) A nonbonding *s* orbital on the nitrogen atom.

VI. TRIVALENT NITROGEN

Nitrogen in the trivalent state can have associated with it a number of different combinations of σ and π bonds. These will be dealt with in a systematic manner in the following sections.

A. Three σ bonds

For the pyramidal molecule NH_3, provided each HNH angle is 90°, the lowest-energy molecular orbitals are:

(i) Three σ-type bonding molecular orbitals. Each orbital is localized in a particular nitrogen–hydrogen bond and is formed by the overlap of a 1*s* atomic orbital of hydrogen with a 2*p* atomic orbital of nitrogen.

(ii) An orbital localized on the nitrogen atom, closely resembling an atomic 2*s* orbital of nitrogen. This molecular orbital is nonbonding.

B. Two σ bonds, one π_L bond

When the nitrogen atom is attached to a divalent group X and to a univalent group Y the lowest-energy molecular orbitals that can be formed are:

(i) Two localized σ-type bonding orbitals built from pure p atomic orbitals of the nitrogen atom together with suitable atomic orbitals from atoms X and Y.

(ii) A π-type molecular orbital compounded by the overlapping of two atomic orbitals, one on the nitrogen atom and one on X. This is of the form given by equation 1.

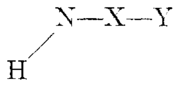
(iii) A nonbonding orbital localized on the nitrogen atom.

(iv) Nonbonding orbitals localized on the atoms X and Y.

The nitrogen atom is trivalent and its type of bonding may be symbolized as $N(2\sigma, \pi_L)$.

C. Two σ bonds, one π_D bond

In a molecule of the type



the three atoms N, X, and Y are collinear and the hydrogen atom is off-axis; the four atoms are then necessarily coplanar. If both X and Y possess $2p\pi$ atomic orbitals, the lowest-energy molecular orbitals concerned with the bonding in the molecule are:

(i) Three localized σ-type bonding orbitals constructed from the appropriate atomic orbitals of the atoms present. Since the NXY grouping is linear, the sp hybridization of X is involved.

(ii) A localized π-type bonding molecular orbital connected with atoms X and Y and lying in the plane of the molecule.

(iii) Delocalized π-type molecular orbitals extending over the three nuclei owing to the overlapping of three $p\pi$ atomic orbitals one on each of the atoms N, X, and Y. These molecular orbitals will have the form

$$\psi = l\phi(\mathrm{N}:2p) + m\phi(\mathrm{X}:xp) + n\phi(\mathrm{Y}:yp)$$

Mulliken (56) has shown that for a linear grouping the two lowest-energy molecular orbitals have $l = n$, $m \approx n$, leading to a bonding molecular orbital extending over the three nuclei, and $l = -n$, $m = 0$, producing a molecular orbital which involves the end atoms only. This orbital is N↔Y antibonding but since these atoms are relatively far apart it gives neither antibonding nor bonding between X and the adjacent atoms.

(iv) Lone-pair orbitals associated with the atoms N and Y.

D. One σ bond, two π_L bonds

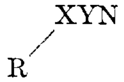
In molecules such as the cyanides where nitrogen is combined with a trivalent group, one σ bond and two localized π bonds are formed by the feeding in of electrons to the appropriate molecular orbitals. For such systems the lowest-energy molecular orbitals associated with the nitrogen atom that can be formed are:

- (i) One σ-type molecular orbital.
- (ii) Two localized π-type molecular orbitals formed from the appropriate $p\pi$-type atomic orbitals of the nitrogen and adjacent atom.
- (iii) A lone-pair orbital associated with the nitrogen atom.

E. One σ bond, one π_L bond, one π_D bond

Molecules such as hydrazoic acid and the azides have a linear grouping terminated by a nitrogen atom.

In molecules of the type



the RX bond and the linear XYN group define a plane. Atoms Y and N possess $p\pi$-type atomic orbitals in this plane, whilst X, Y, and N possess $p\pi$ orbitals at right angles to the plane.

The molecular orbitals of lowest energy that can be formed from the available atomic orbitals are as follows:

- (i) A lone-pair $2s$ orbital on the nitrogen atom.
- (ii) Three σ-type bonding orbitals built from sp hybrid atomic orbitals of Y, a suitable σ-type atomic orbital of R, and the $p\sigma$ atomic orbitals of X and N. The bonds corresponding to these molecular orbitals are localized to a large extent between the atom pairs RX, XY, and YN.
- (iii) A localized π_L-type molecular orbital arising from the in-phase overlap of the in-plane $p\pi$ atomic orbitals on the Y and N atoms.
- (iv) A delocalized π_D-type molecular orbital arising from the in-phase overlap of the out-of-plane $p\pi$ atomic orbitals on the X, Y, and N atoms. This molecular orbital is bonding.
- (v) A π^*-type molecular orbital arising from the X, N in-phase, Y out-of-phase overlap of the out-of-plane $p\pi$ atomic orbitals on the X, Y, and N atoms. This orbital is X↔N bonding to some extent but X↔Y, Y↔N antibonding.

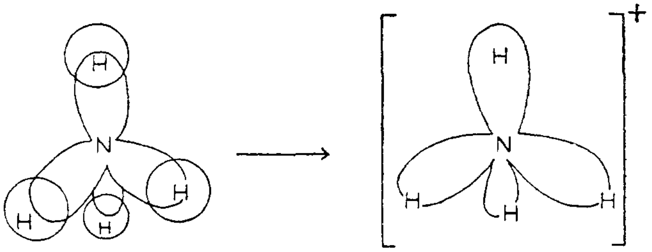
VII. QUADRIVALENT NITROGEN

In a discussion of the electronic structure of hydrazoic acid, HN_3, it has been shown that the central nitrogen atom is quadrivalent (62) and not quinquevalent as postulated by Samuel (74–79). The quadrivalent valence states of the nitrogen atom can be visualized as arising from the following schemes:

From the N^+ *ion*

$$\underset{\text{Ground state}}{N^+[1s^22s^22p^2]} \quad \rightarrow \quad \underset{\text{Excited state}}{(N^+)^*[1s^22s^22p^3]} \quad \xrightarrow[\text{hybridization}]{sp^3} \quad \underset{\text{Valence state}}{N^+[(1s)^2(2sp^3)^4]}$$

The four $2sp^3$ hybrid atomic orbitals of nitrogen may be used to form molecular orbitals with other suitable atomic orbitals which on being filled with electrons lead to the formation of four σ bonds.



From the N *atom*

$N[(1s)^2(2s)^2(2p)^3]$ Ground state

↓

$N^*[(1s^2)(2s)(2p)^4]$ Excited state

sp^2 hybridization ↙ ↘ sp hybridization

$N[(1s)^2(2sp^2)^3(2p)^2]$ Valence states $N[(1s)^2(2sp)^2(2p)^3]$

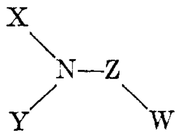
The sp^2-hybridized nitrogen atom can utilize its hybrid atomic orbitals to form σ-type molecular orbitals; the pure $2p$ atomic orbital of nitrogen can help form a π-type molecular orbital. Similarly the sp hybrids of the digonal-hybridized nitrogen atom can form σ-type molecular orbitals, whilst the $2p$ atomic orbitals of nitrogen can be combined with other suitable $p\pi$ atomic orbitals to form π molecular orbitals.

A. Four σ bonds

In molecules such as ammonium chloride and in amine oxides the nitrogen atom is attached to four atoms. The lowest-energy molecular orbitals that can be formed are four σ-type bonding orbitals formed by the overlapping of the four $2sp^3$ atomic orbitals of nitrogen with suitable atomic orbitals from the four attached atoms.

B. Three σ bonds, one π_D bond

When nitrogen in the sp^2-hybridized state is combined with atoms in an all-planar grouping, e.g.,



then the lowest-energy bonding molecular orbitals of molecules containing such a grouping number amongst others:

(i) Three σ-type molecular orbitals visualized as being formed from sp^2 hybrid atomic orbitals of nitrogen and suitable atomic orbitals from the atoms X, Y, and Z.
(ii) A π-bonding molecular orbital arising from the considerable overlap of pure p orbitals on the nitrogen and other adjacent atoms.
(iii) A π^*-nonbonding molecular orbital formed from the $p\pi$ atomic orbitals on the nitrogen and adjacent atoms.

The lone-pair electrons originally with configuration $N(2s)^2$ are in a pure p orbital when the atom is sp^2 hybridized. These electrons may be fed into the π- and π^*-type molecular orbitals described above.

C. Two σ bonds, two π bonds

When the nitrogen atom is the central atom in a linear triatomic grouping X—N—Y, where X and Y are divalent groups, the lowest-energy molecular orbitals pertaining to the nitrogen atom, assuming that they are compounded from s and p atomic orbitals, are:

(i) Two σ-type molecular orbitals formed from nitrogen sp hybrids with suitable atomic orbitals from X and Y.
(ii) Two π-type molecular orbitals formed by the overlap of atomic p orbitals on X and N and Y. Depending upon the number of π electrons available and the molecular environment these molecular orbitals can be localized or delocalized bonding molecular orbitals; another possibility is an X↔Y antibonding molecular orbital.

D. Two σ bonds, two delocalized π bonds

In linear molecules XNY, such as nitrous oxide, the central nitrogen atom is sp hybridized. The lowest-energy molecular orbitals are:

(i) An atomic nonbonding X:xs orbital.
(ii) An atomic nonbonding Y:ys orbital.
(iii) Two bonding σ-type molecular orbitals formed from the $2sp$ atomic orbitals of nitrogen and the appropriate X:xp and Y:yp atomic orbitals.
(iv) Two bonding π_D-type molecular orbitals embracing the three nuclei.
(v) Two antibonding π^*-type molecular orbitals. These are mainly associated with the terminal atoms X and Y. Since these atoms are relatively far apart, these orbitals when filled have little effect on the bonding.

VIII. DISCUSSION OF SPECIFIC NITROGEN COMPOUNDS

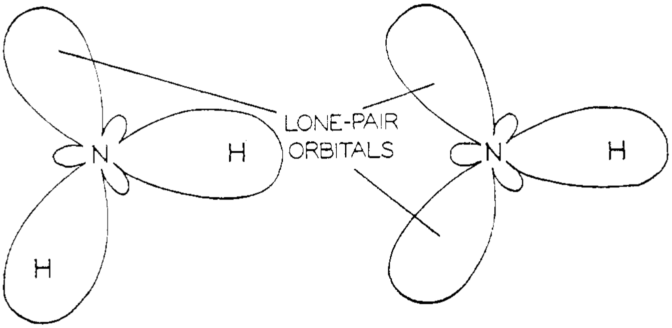
A. Amide ion and amido radical

The metallic amides, MNH_2, are ionized compounds, $M^+(NH_2)^-$. They contain the anion NH_2^-, which possesses eight valence electrons.

The four molecular orbitals described in Section IV suffice to hold the eight valence electrons possessed by the system. The ion is nonlinear and isoelectronic with H_2O. In H_2O it is known that the atomic orbitals of the oxygen atom used in conjunction with the $1s$ atomic orbitals of hydrogen to form the bonds are not pure p but partake of some s character. The valence state of the nitrogen in the amide is then best represented as

$$N^-[(1s)^2(2s + \delta 2p)^4(2p + \delta 2s)^2]$$

where the lone-pair electrons are now in hybrid orbitals, $(2s + \delta 2p)$. These nonbonding lone-pair orbitals, since they have directional character, form "atomic" dipoles, a term introduced by Coulson. The molecule can be pictured thus:



Herzberg and Ramsay (35) have described the absorption spectrum for free NH_2 radicals. They showed that the molecule was an asymmetric top with small moments of inertia, i.e., the molecule is nonlinear. This paramagnetic molecule has one electron less than the NH_2^- ion. The molecular orbital description is then the same, but one of the lone-pair orbitals contains only one unpaired electron.

B. Ammonia

The ammonia molecule possesses eight valence electrons, and these suffice to fill the four molecular orbitals described in Section VI,A.

The ammonia molecule is pyramidal in structure, since it has a dipole moment (41) of value $\mu = 1.44$. The absorption spectrum (3) also indicates a pyramidal form, with $r(\text{NH}) = 0.94$ A. and $\angle \text{HNH} = 109°$. This deviation from the ideal value of 90° is due to the mutual repulsions of the hydrogen atoms and to hybridization changes at the nitrogen atom. The valence state of the nitrogen atom in the pyramidal configuration may be represented as

$$N[(1s)^2(2s + \delta 2p)^2(2p + \delta 2s)^3]$$

i.e., the lone-pair electrons originally with configuration $N{:}(2s)^2$ are actually present in a hybridized molecular orbital, thus producing an atomic dipole. This atomic dipole provides the major part of the total dipole moment of the molecule, since the intrinsic polarities of XH bonds are small (53).

The presence of an atomic dipole at the nitrogen atom is of great importance in the formation of hydrogen bonds. In this respect ammonia bears a considerable resemblance to water. In the liquid state both substances are associated. It has been shown also, by means of infrared studies, that gaseous ammonia is associated (73).

The predominating influence of atomic dipoles in determining the values of dipole moments is emphasized by a comparison of the electronic structures of NH_3 and NF_3. Since the bond angles at the nitrogen atom do not differ greatly, the state of hybridization of the nitrogen atoms in the two molecules is presumably much the same. On simple grounds the dipole moment of NF_3 would be expected to be greater than that for NH_3. The bond moments of N—H and N—F links are in opposite directions. It seems then that the small dipole moment (0.2 D) of NF_3 can only be accounted for by the compensation of the moment of the polar NF_3 grouping by the atomic dipole arising from the lone-pair electrons on the nitrogen atom.

C. Amines; hydroxylamines

In ammonia the nitrogen hybrid orbitals used in the formation of σ bonds are equivalent and may be represented as $N(2p + \delta 2s)$. When the atoms or groups attached to the central nitrogen atom are dissimilar the hybrids are nonequivalent, i.e., their degrees of hybridization are different.

For primary amines, RNH_2, and hydroxylamines of the type $RONH_2$ the valence state of the nitrogen atom may be symbolized as:

$$N[(1s)^2(2s + \delta 2p)^2(2p + \delta' 2s)^2(2p + \delta'' 2s)^1]$$

The $N(2p + \delta' 2s)$ atomic orbitals, being equivalent, would form localized bonding molecular orbitals with the $1s$ atomic orbitals of hydrogen. The atomic orbital having a different s/p ratio ($\delta' \neq \delta''$) would, in conjunction with an appropriate orbital of the adjoining group, form a third localized molecular orbital.

For secondary amines the picture is similar when both alkyl substituents are the same. When they are different, as in RR′NH, then the three hybrid atomic orbitals are nonequivalent and may be represented as:

$$\phi = p + \lambda_i s \quad (i = 1, 2, 3)$$

The three σ bonds are formed by the overlapping of the three singly occupied atomic orbitals with the appropriate bond-forming atomic orbitals of the hydrogen atom and of the radicals R and R′.

When the hybrid orbitals are nonequivalent no simple relation exists between interbond angles and the s/p hybridization ratios.

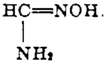
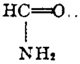
The tertiary amines can be described in an exactly similar manner.

Some NH_2 bond-stretching frequencies of monomeric molecules are given in table 3. In hydroxylamine, *O*-methylhydroxylamine, ammonia, and methylamine the valence bonds of the nitrogen atom are not coplanar. The interbond angles are near to the tetrahedral value, indicating that the nitrogen atom is approximately sp^3 hybridized. The nitrogen–hydrogen bonds, then, have some 25 per cent s character.

Recent microwave (44) and infrared studies (66) have shown that the nitrogen valence bonds in formamide and in formamidoxime are planar. There are also grounds for believing that the nitrogen valencies are planar, or very nearly so, in aniline (15). In these compounds the nitrogen atom will be very nearly sp^2

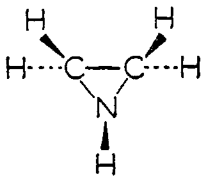
TABLE 3

NH_2 *stretching frequencies*

Molecule	State	$\nu_a(NH_2)$	$\nu_s(NH_2)$	References
		cm.$^{-1}$	*cm.*$^{-1}$	
H_2NOH	Vapor	3350 (?)	3297	(24)
H_2NOCH_3	Vapor	3414	3269	(66)
NH_3	Gas	3414	3337	(28)
H_2NCH_3	Vapor	3425	3360	(55, 66)
 $\underset{NH_2}{\underset{\vert}{HC}}{=}NOH$	Solution in CCl_4	3530	3424	(56)
 $\underset{NH_2}{\underset{\vert}{HC}}{=}O$	Vapor	3545	3450	(21)
$C_6H_5NH_2$	Vapor	3497	3416	(66)

hybridized and the bonds will possess some 33⅓ per cent *s* character. This increase in *s* character tends to shorten the nitrogen–hydrogen bonds and accounts for the higher values found for the NH stretching frequencies.

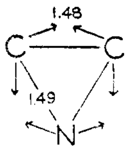
D. Ethylenimine



Preliminary analyses of the microwave spectrum of ethylenimine have been reported, and tentative structural data have been given (88, 93). By assuming reasonable values for the other parameters the following dimensions were determined:

r(CC)	1.480 A.
r(CN)	1.488 A.
C_2NH angle	112°

According to the microwave data the CCN and CNC angles are sensibly equal, with a value of 60°. The bonding here, then, is similar to that found in cyclopropane and in ethylene oxide; the isoelectronic groups $H_2C\langle$, $HN\langle$, and $O\langle$ bear a resemblance to each other and the structural features of a series of molecules, identical except for these groups, are somewhat similar. (For example, in the series $CH_2N'N''$, $HNN'N''$, $ON'N''$ the length of the $N'N''$ bond varies but little; the two bond-stretching force constants associated with the linear triatomic grouping have values near each other, etc.) Since no two *sp* hybrid atomic orbitals may be at an angle less than 90° to each other, the carbon and nitrogen hybrids in the plane of the CCN skeleton cannot point directly at each other.

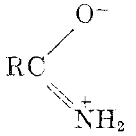


By pairing together the adjacent orbitals which point towards each other, bent molecular orbitals may be formed which form "banana" bonds on the introduction of the bonding electrons. This description was introduced by Coulson to differentiate between this type of "strained" bond and the π-type "sausage" bond. Whilst the detailed representation of such molecular orbitals involves many approximations, the disposition of the atomic orbitals is such that a "banana" type of electron distribution is certainly involved.

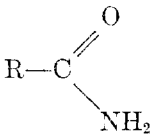
E. Amides

The amides have a more complex electronic structure than the amines; however, to a somewhat poorer approximation the nitrogen bonding may be described as being three σ bonds.

In valence-bond discussions of amide structure the importance of an ionic form has been stressed. This may be formulated as:



One important point about the ionic form of the valence-bond amide structure is that the quadrivalent nature of the nitrogen atom makes the atoms $OCNH_2$ coplanar, the carbon–nitrogen bond consisting of a σ bond and a localized π bond which must necessarily be at right angles to the OCN plane. Bates and Hobbs (5), however, have demonstrated that the normal covalent structure



is capable of accounting for almost all the observed dipole moments by vector addition of accepted bond moments. However, when the carbon–nitrogen bond lengths, bond frequencies, and force constants of amides and amines are compared, it is clear that some modification of the state of hybridization of the nitrogen atom has occurred. This change in the degree of hybridization of a nitrogen atom, which is predominantly trivalent, is emphasized by the significant changes in the same parameters for the NH_2 group. The following data (in the normal units) refer to methylamine and formamide.

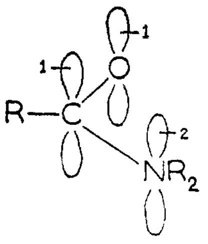
	$r(CN)$	$f(CN)$	(CN)	$r(NH)$	$\nu_a(NH_2)$	$\nu_s(NH_2)$	$f(NH)$	$\delta(NH_2)$	References
CH_3NH_2	1.47	4.6	1045	1.02	3410	3360	6.3	1625	(8, 67)
$HCONH_2$	1.4	6.2	1253	1.00	3545	3450	6.8	1572	(25, 63)

In methylamine the nitrogen valence bonds are pyramidal, the interbond angles having approximately the tetrahedral value. The microwave spectrum of formamide indicates that the nitrogen valence bonds are planar, the NH_2 group being in the plane of the rest of the molecule (44). In methylamine then, the nitrogen atom is approximately sp^3 hybridized, whilst in formamide it is near to being sp^2 hybridized. This change in hybridization on going from a nonplanar to a planar configuration of the nitrogen valence bonds accounts in a satisfactory way for the differences found in the comparable molecular parameters of methylamine and formamide. The values quoted above and in table 3 show that the NH_2 bond-stretching frequencies afford a sensitive criterion concerning the planarity or otherwise of nitrogen valence bonds.

The carbon–nitrogen bond length in formamide has been estimated as 1.40 A. (24). This represents a contraction of some 0.07 A. when compared with the "normal" carbon–nitrogen single bond of 1.47 A. This contraction is partly due to the contraction of the atomic radii of the carbon and nitrogen atoms, owing to their state of hybridization, and partly to the carbon–nitrogen bond acquiring some π-bond character. The all-planar configuration of formamide affords the maximum opportunity for the formation of delocalized π-bonding in the OCN grouping. The bond length/bond order relation (figure 1) indicates a bond order of 1.36 for the carbon–nitrogen link in formamide. This accounts for the increased carbon–nitrogen force constant found in formamide as compared with methylamine (63).

In substituted amides, amides in the liquid and solid states (i.e., associated amides), and polymers containing the amide grouping much greater contractions of carbon–nitrogen bond length occur. In these cases the carbon–nitrogen bond has appreciable double-bond character and the nitrogen valence bonds tend to become coplanar with the OCN grouping. It seems, therefore, that in amides in the vapor state and also in condensed phases the nitrogen atom is quadrivalent (three σ bonds, one π_D bond).

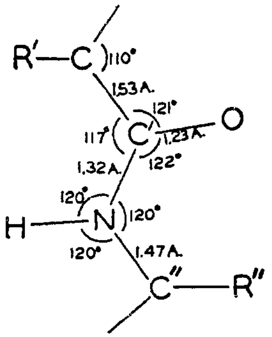
When the nitrogen atom in an amide is sp^2 hybridized, one $N(2p)$ atomic orbital is unchanged. If the NH_2 (NHR or NR_2) group is coplanar with the OCN group, diagrammatically the distribution of the four π electrons is



The oxygen, carbon, and nitrogen $2p\pi$ atomic orbitals shown contain four electrons. With this configuration maximum overlapping of the $2p\pi$ atomic orbitals occurs with the formation of π-type molecular orbitals embracing the OCN grouping. The lowest-energy molecular orbitals have been described in Section VI,B. The four $2p\pi$ electrons just suffice to fill the bonding molecular orbital embracing the OCN grouping and the O↔N nonbonding orbital. The net effect is a decrease in π-bond order in the carbon–oxygen link with a compensating increase in π-bond order in the carbon–nitrogen link. It is emphasized that for the appreciable formation of this delocalized π-bonding the nitrogen atom must be near the sp^2-hybridized state and that the OCN and NH_2 (NHR, NR_2) groups be coplanar.

In such an environment the nitrogen atom is quadrivalent (three σ bonds, one π_D bond). Depending on the relative values of the coefficients of the atomic orbital type wave functions in the bonding molecular orbital, which in turn will depend on the environment of the nitrogen atom, the bond orders of the carbon–oxygen and carbon–nitrogen links can vary in a continuous manner. When the coefficients are sensibly equal, the π-bond orders in the adjoining bonds will be sensibly equal and have a value of about 0.5. This is in agreement with Cox and Jeffrey (17), who point out that carbon–nitrogen π-bond orders of less than 0.5 are unknown in systems where nitrogen is in the sp^2 valence state and is adjacent to an unsaturated carbon atom; i.e., the π-bonding in such cases extends considerably to the carbon–nitrogen link.

On the basis of extensive and detailed x-ray studies of amides and peptides, Pauling and Corey (68, 69) have shown that the (RCONR′) residues are planar. The observed shorter carbon–nitrogen bond distance, 1.32 A., corresponds to a bond order of 1.8. The interatomic distances and bond angles within the residue based on crystallographic work are as follows (12):



In a system such as this the *a priori* conditions for maximum overlapping of $2p\pi$ atomic orbitals on the oxygen, nitrogen, and carbon atoms exist, and it is clear from the bond-length values obtained that delocalized molecular orbitals are involved. The bond-length values quoted indicate that the delocalized molecular orbitals are confined to the grouping OC′N, since the values obtained for the C—N″ and C—C bond lengths indicate that they are pure single σ bonds. There is no evidence that mobile σ electrons spread to these latter linkages.

The nitrogen atom in methylamine is trivalent, the carbon–nitrogen bond being pure σ in type. The evidence quoted indicates, however, that amides in the vapor, liquid, and solid states possess a quadrivalent nitrogen atom.

It has been pointed out by Davies and Orville-Thomas (20) that significant variations occur in the carbon–oxygen bond orders in the carboxyl group as the environment changes (vapor, solution, liquid, solid); these variations are quite independent of the changes resulting from dimerization. Similar changes occur in amides on change of phase. Spectroscopic results indicate that the π-bond character of the carbon–nitrogen bonds in amides depends upon the environment of the molecule (24). As the π-bond order of the carbon–nitrogen link increases, that of the carbon–oxygen link decreases. Evidence for this is provided by the change in carbon–oxygen and carbon–nitrogen bond-stretching frequencies as one goes from the vapor to solutions or to the liquid state.

F. Nitrous acid; alkyl nitrites (RONO)

The infrared spectrum of gaseous nitrous acid has been investigated and, using the experimentally determined rotational constants, probable values of the molecular parameters were obtained (39).

	cis-HONO	*trans*-HONO
$r(N—O)$	1.46	1.46
$r(N=O)$	1.20	1.20
∠ONO	114°	118°

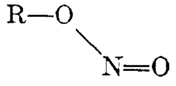
Kohlrausch and his coworkers (42, 43) have shown that alkyl nitrites have two strong Raman shifts centered at 1600 and 600 cm.$^{-1}$ D'Or and Tarte (21) have obtained the infrared spectra of a number of nitrites in the gaseous state. All the spectra exhibit strong absorptions in the regions 1660, 800, and 600 cm.$^{-1}$ These frequencies are assigned to the two bond-stretching and the bond-bending vibrations of the ONO group:

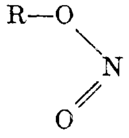
$$\nu(\mathrm{N{=}O}) \text{ or } \nu_a(\mathrm{O{-}N{=}O}) = 1660 \text{ cm.}^{-1}$$

$$\nu(\mathrm{N{-}O}) \text{ or } \nu_s(\mathrm{O{-}N{=}O}) = 800 \text{ cm.}^{-1}$$

$$b(\mathrm{O{-}N{=}O}) = 600 \text{ cm.}^{-1}$$

In all nitrites studied the bands centered at 1660 and 600 cm.$^{-1}$ are double; in addition, for the first members of the series (methyl, ethyl, and propyl) the 800 cm.$^{-1}$ bond is also double. This has been explained on the basis of rotational isomerism. It is suggested that the molecule can exist in the following two configurations:





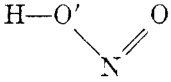
This supposition is strengthened by observations on the temperature dependence of the bands. The cis form, where the lone-pair interaction is the greater, is of higher energy by about 506 cal. mole.$^{-1}$ Nitrous acid, then, differs from the isoelectronic molecule formic acid, in which the trans form has higher energy, i.e., the cis form is the more stable; the trans form of formic acid has not been found to exist under the experimental conditions so far investigated. Nitrous acid does not associate at pressures at which dimeric formic acid is found.

The formation of the HONO molecule can be pictured as follows. Since the nitrogen atom is attached to two oxygen atoms it is reasonable to suppose that the σ-bond-forming atomic orbitals of nitrogen are equivalent. The ONO angle of 116° indicates that the nitrogen atom is essentially in the sp^2-hybridized state. Two $N(2p + \delta 2s)$ atomic orbitals form σ bonds with the oxygen atoms; the lone-pair electrons are in the hybrid $N(2s + \delta 2p)$ orbital and form an atomic dipole. The valence states for the other atoms may be taken to be:

$H(1s)$

$O'(1s^2 2s^2 2p_x 2p_y 2p_z^2)$

$O''(1s^2 2s^2 2p_x 2p_y^2 2p_z)$



σ bonds are formed as indicated by the following wave functions, which represent bonding molecular orbitals.

$$\psi = a\phi H(1s) + b\phi O'(2p_x)$$

$$\psi = c\phi O'(2p_y) + d\phi N(2p + 2s)$$

$$\psi = e\phi N(2p + 2s) + f\phi O''(2p_x)$$

The atoms O′, N, and O″ have $2p_z$ atomic orbitals which are at right angles to the xy, O′NO″ plane. These may be used to build up molecular orbitals of the general form:

$$\psi = l\phi(X{:}2p_z) + m\phi(N{:}2p_z) + n\phi(Y{:}2p_z) \tag{2}$$

There are four electrons remaining to be fed into molecular orbitals of this type.

The bond lengths and vibrational frequencies of the ONO grouping indicate that two of these electrons are situated in a bonding molecular orbital forming a localized π bond between atoms N and O″, and two in an O′↔O″ nonbonding orbital.

The $\nu(N{=}O)$ frequency is considerably below the corresponding frequency in the NOX molecules (X = F, Cl, Br); similarly, $r(N{=}O)$ in HONO is greater than $r(N{=}O)$ in the NOX series; in addition, the N—O single-bond length is greater than the "normal" single-bond value for this link. These facts indicate that, even though the oxygen atoms are relatively far apart, the O′↔O″ nonbonding molecular orbital is to some extent antibonding, i.e., it weakens the bonding in the ONO grouping.

TABLE 4

Molecular parameters for HNXY *molecules*

Parameter	HNCO	HNCS	$HN_1N_2N_3$	Parameter	HNCO	HNCS	$HN_1N_2N_3$
	A.	*A.*	*A.*		*10^5 dynes/cm.*	*10^5 dynes/cm.*	*10^5 dynes/cm.*
r_1	0.987	1.013	1.021	$f(r_1)$	6.9	7.0	6.2
r_2	1.207	1.216	1.240	$f(r_2)$	14.0	13.2	10.1
r_3	1.171	1.561	1.134	$f(r_3)$	15.0	7.27	17.3
α	128°5′	130°32′	112°39′	$f(\Delta r_2/\Delta r_3)$	1.32	0.75	1.74
				$N(r_2)$	2.37	2.26	1.58
				$N(r_3)$	2.18	2.00	2.40

G. Isocyanic, isothiocyanic, and hydrazoic acids

Cyanic acid and thiocyanic acid exist in the form HNCY, i.e., they have the imide structure and are thus correctly called isocyanic and isothiocyanic acids. The configuration of HNCO has been deduced by Herzberg and Reid (36) from the fine structure of the infrared vibrational bands. The molecular parameters are given in table 4 together with those obtained from infrared (19, 26) and microwave studies of HN_3 and HNCS (1, 6). From a consideration of the class A′ vibrations, reasonable sets of force constants have been obtained for these molecules (62). Values for the bond orders of the hybrid links have been obtained using these force constants in conjunction with Gordy's empirical relation connecting force constant and bond order (30). These values are incorporated in table 4. The molecules are represented in general form by figure 6.

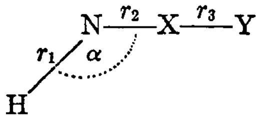


FIG. 6. Configuration of the HNXY molecule

The HNX angle varies between 112° and 138°. This departure from the ideal value of 90° indicates that the σ-bond-forming orbitals of the nitrogen atom contain appreciable *s* character, and that its lone-pair electrons necessarily form atomic dipoles.

The bond-stretching force constants and bond orders given in table 4 confirm the existing evidence that the molecules HNCO and HNCS have the form HNCY and not the alternative enol and thiol forms (6, 33, 36, 95). In the latter case the carbon–nitrogen force constants and bond orders should approach normal triple-bond values; viz., 18×10^5 dynes per centimeter and 3. The values obtained however, indicate that the carbon–nitrogen link is nearer a double bond in character.

The bond-stretching force constants obtained for the nitrogen–nitrogen links in hydrazoic acid ($HN_1N_2N_3$) mirror in a quantitative form the difference between the nitrogen–nitrogen bonds. The corresponding bond-order values, $N_1N_2 = 1.6$, $N_2N_3 = 2.4$, indicate that considerable delocalization of π electrons occurs. This is emphasized by the large positive value obtained for the (N_1N_2/N_2N_3) bond-bond interaction constant. Using Coulson's definition of bond order (13) we see that the N_2N_3 π-bond order exceeds that of N_1N_2 by 0.8.

The value obtained for f(HN) is considerably lower than those found in HNCO and HNCS. This suggests that the N_1 σ-bonding orbital to hydrogen contains less s character than the corresponding bonds in HNCO and HNCS. This is also indicated by the value found for r(HN), viz., 1.021 A., which is some 10 per cent longer than the values quoted for the other molecules.

A molecular orbital description of the distribution of the valence electrons in these molecules has been given by Orville-Thomas (62).

The trivalent nitrogen atom bound on one side to hydrogen has associated with it two σ-bonding molecular orbitals and a delocalized π-bonding molecular orbital (Section VI,C). The terminal atoms, Y, have associated with them one σ-type, one localized π-type, and the delocalized π orbital mentioned above—this embraces the three atoms N, X, and Y. In addition the N and Y atoms have a lone pair of electrons in a hybridized orbital and also an N↔Y antibonding π^*-type molecular orbital. The orbitals described suffice to hold the sixteen valence electrons possessed by the molecules. In hydrazoic acid the central quadrivalent nitrogen atom, which is sp hybridized, has associated with it two σ bonds, a localized π bond, and a delocalized π bond. The bond-order values quoted in table 4 indicate that in HNCO and in HNCS the π_D bond is localized to a greater extent between the N and X atoms than is the case in HN_3.

The best force constants which can be chosen from a quadratic potential function of methyl azide have recently been determined (40). In units of 10^5 dynes per centimeter the bond-stretching force constants are $f(N_1N_2) = 9.4$ and $f(N_2N_3) = 17.3$. These values indicate that no great change in the electronic structure of the linear grouping occurs in going from hydrazoic acid to its methyl derivative. The value of $f(CN_1) = 4.5 \times 10^5$ dynes per centimeter for the $H_3C—N_1$ bond shows that this off-axis link is a pure σ bond. Hyperconjugation effects, if they exist, are of small import.

H. Nitrogen peroxide

In the solid state nitrogen peroxide exists as the dimer N_2O_4; partial dissociation to NO_2 takes place in the liquid and at 100°C. the vapor is 90 per cent monomer (27).

The structure of NO_2 was deduced by Sutherland and Penney (85, 86). They showed from the contours of the absorption bands that the molecule was nonlinear. The molecular parameters, $r(NO) = 1.20$ A., $\angle ONO = 132°$, have been determined by means of electron diffraction studies (7, 51).

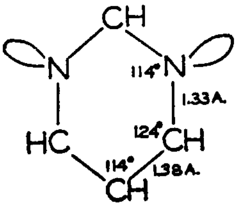
Since the $\angle$ONO is much nearer 120° than 90° the nitrogen atom is approximately in the sp^2 state of hybridization; σ bonds are formed by the feeding in of electrons to molecular orbitals localized between the nitrogen and oxygen atoms. In addition to the ten lone-pair electrons there are three $2p\pi$ electrons which probably form a three-electron bond, associated with the three nuclei. In the same manner as for nitric oxide this bond will give a certain amount of π-bond character to the nitrogen–oxygen links. The total bond order, then, will be greater than 1 but less than 1.5. This corresponds to the bond length 1.20 A., which lies between the normal N—O value of 1.43 A. and 1.16 A. for N=O.

It has been established by Bennett, Westheimer, and Kharasch and Ingold, Hughes, and their coworkers that the nitrating agent present in a solution of nitric acid in concentrated sulfuric acid is the NO_2^+ cation. This ion may be visualized as being obtained from NO_2 by the ionization of the odd electron in the antibonding π^* orbital, thus reducing the three-electron bond to a more usual two-electron delocalized π bond. NO_2 is nonlinear but the ion NO_2^+ is linear (29), in common with all XY_2 molecules containing sixteen or less valence electrons in their ground states. Since NO_2^+ and CO_2 are isoelectronic, the description of the chemical bonding in these molecules is very similar.

I. Pyrimidine

The description of the valence bonding of the nitrogen atom in NO_2, viz., N(two σ, π_D) is essentially the same in compounds such as pyrimidine, where three bonding π-type molecular orbitals are associated with the six atoms forming the nucleus of the molecule.

From a consideration of the results obtained for substituted pyrimidines Clews and Cochran (9) have predicted for pyrimidine itself the following configuration.



The carbon–nitrogen bond length of 1.33 A., corresponding to a bond order of 1.68, indicates appreciable double-bond character. The CNC angle of 114° shows that the nitrogen atom is almost in the trigonal valence state. Two of the hybrids form σ bonds to carbon atoms. The third hybrid orbital contains the lone-pair electrons whose original configuration was $N:2s^2$. The single electron, originally in the $N:2p\pi$ atomic orbital, is fed into a delocalized molecular orbital. The slight difference in bond length between the carbon–carbon bonds of pyrimidine and those of benzene (1.39 A.) suggests that the charge distributions in those two systems are very similar, each possessing six $2p\pi$ electrons.

J. Nitrogen; cyanide ion; nitric oxide

Using the abbreviated notation introduced by Mulliken (55) the formation of molecular nitrogen (N_2) can be pictured as follows

$$N[1s^2 2s^2 2p^3] + N[1s^2 2s^2 2p^3] \rightarrow N_2[KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4]$$

TABLE 5

Molecular parameters for XCN *molecules*

Molecule	Bond Lengths			Bond-stretching Frequencies		Force Constants	
	r(CN)	r(CX) (observed)	r(CX) (calculated)	ν(CN)	ν(CX)	f(CN)	f(CX)
	A.	*A.*	*A.*	*cm.*$^{-1}$	*cm.*$^{-1}$	*10^5 dynes/cm.*	*10^5 dynes/cm.*
HCN	1.153	1.066	—	2095.5	3311.68	18.58	6.29
CH_3CN	1.158	1.460	—	2267	919.1	18.0	5.2
ClCN	1.163	1.630	1.76	2201	729	17.61	5.01
BrCN	1.160	1.789	1.91	2187	580	17.80	4.10
ICN	1.159	1.995	2.10	2158	470	17.94	2.92

The symbol KK means that both K shells are fully occupied. Since the $z\sigma$ molecular orbital is bonding, whilst the $y\sigma$ orbital is antibonding to the same extent, the binding is effectively due to the six electrons in the bonding molecular orbitals $x\sigma$ and $w\pi$, i.e., N_2 possesses a triple bond.

Similarly, the heteronuclear ion CN^-, which is isoelectronic with N_2, can be portrayed as

$$CN^-[KK(C:2s)^2(N:2s)^2(\sigma 2p)^2(\pi 2p)^4]$$

which illustrates an alternative notation for the description of molecular orbitals.

The "free radical" nitric oxide can be described in the following terms:

$$NO[KK(N:2s)^2(O:2s)^2(\sigma 2p)^2(\pi 2p)^4(\pi^* 2p)^1]$$

The filled orbitals $(\sigma 2p)^2$ $(\pi 2p)^4$ correspond to a triple bond; the orbital $(\pi^* 2p)$ is antibonding and its single electron reduces the net π-bonding to the order of 1.5, i.e., the total bond order is approximately 2.5.

When the antibonding $\pi^* 2p$ electron is removed, the ion NO^+ is produced. As is to be expected, the bonding in this ion is stronger than that in the molecule, possessing as it does one σ bond and two π bonds. In addition, when the antibonding $\pi 2p^*$ electron is excited to a relatively nonbonding molecular orbital, the excited NO molecule behaves as if it had a triple bond.

Experimentally it is found that the dipole moment of nitric oxide has a very small value, $\mu = 0.16$ D (91). As indicated by Coulson, this can be explained in much the same way as the low dipole moment of carbon monoxide. The nitrogen lone-pair electrons are in a hybrid $(2s + \delta 2p)$ orbital and so will give rise to an atomic dipole in the molecule. This atomic dipole will tend to cancel the polar effect due to asymmetry of charge in the nitrogen–oxygen bonds.

K. Cyanogen derivatives

The bond lengths, force constants, and bond-stretching frequencies for some X—C≡N molecules are given in table 5. The data given in this table indicate in a clear fashion that the carbon–nitrogen links in these molecules have typical triple-bond values; these molecules afford examples of triple bonds where six electrons are shared by the carbon and nitrogen atoms.

HCN has a high dipole moment, 2.6 D in benzene solution and 2.93 D in the vapor (83, 90). It seems likely that the nitrogen lone-pair electrons are situated in a hybridized orbital forming an "atomic dipole," which contributes significantly to the total dipole moment of the molecule.

Hydrogen cyanide gives rise to two isomeric series of esters, the nitriles $RC\equiv N$ and the isonitriles $RN\equiv C$. Hydrogen cyanide is not, however, a tautomeric substance (*cf.* HNCO, HNCS). In the isonitriles the nitrogen atom is quadrivalent (two σ, two π_L) and becomes the seat of a positive charge, $R—\overset{+}{N}\equiv\overset{-}{C}$; it is probably this charge distribution which makes it far less favored for the electropositive hydrogen.

A comparison of the molecular parameters for the two types shows that the carbon–nitrogen bond is a triple link in both, the carbon–nitrogen link in the nitriles being a little stronger than that of the isonitriles. The energy content of the nitriles is smaller than that of the corresponding isonitriles. Consequently, the alkyl isonitriles change over into the nitriles on heating. The carbon atom in the isonitriles is trivalent and has a lone pair of electrons; it readily goes over to the tetravalent state, forming, for example, isocyanates and isothiocyanates, RNCO and RNCS. The nitriles have higher boiling points than the isomeric isonitriles, in conformity with their larger dipole moments.

When X is a halogen atom chemical evidence is unable to differentiate between the two possible structures $X—C\equiv N\!:$ and $X—N\equiv C\!:$. The physical evidence is, however, quite conclusive in favor of the $X—C\equiv N$ structure. Badger and Woo (4) obtained heats of dissociation from absorption spectra which showed that the halogen was attached to carbon. The carbon–nitrogen links in this series (1.16 A.) have typical triple-bond values but there is a considerable shortening of the XC links from the expected or "calculated" single-bond values given in table 5. This is reflected in the bond-stretching force constants for the CX links. The CX links in the XCN series are considerably stronger than in CH_3X. This strengthening of the CX links has been explained by Duchesne, who postulated that terminal atoms are so modified by their environment that they tend to have the same degree of hybridization as the atom to which they are attached, i.e., in ClCN the chlorine-bond-forming atomic orbital is an *sp* hybrid orbital and not a pure Cl(3*p*) orbital (23). This effect would lead to a decrease in the effective covalent radius of the halogen atom, thus decreasing $r(CX)$ and increasing the bond-stretching force constant. There are four possible reasons for the diminution of the CX bond length as we go from the CH_3X series to the XCN series. They are: (*a*) A decrease in atomic radius of the carbon atom due to its state of hybridization. This will effect a decrease of about 0.04 A. in $r(CX)$. (*b*) A compensating decrease in the atomic radius of the end atom X tending to be in the same state of hybridization as the carbon atom. (*c*) Any delocalization of electrons over the triatomic grouping XCN. It is clear from the CN parameters given in table 5 that such delocalization, if it occurs, is present to a very small extent. When a π bond originally present in a carbon–nitrogen triple bond is completely disrupted, $r(CN)$ alters by some 0.12 A., equivalent to a decrease of unity in the

TABLE 6

Nuclear quadrupole coupling constants of N^{14}

Molecule	Coupling Constant	Molecule	Coupling Constant
	Mc/.second		*Mc./second*
HCN	−4.58	CH_3NC	+0.5
CH_3CN	−4.40	N′N″O	−0.08 (N″)
HC≡C−C≡N	−4.20		

π-bond order. The maximum Δr(CN) in the XCN series is (X = H→F) 0.008 A., which indicates very little "loss" of π electrons from the carbon-nitrogen link. (*d*) Ionic character.

These considerations seem to indicate that in the formation of the XC bond a hybrid X atomic orbital is used which gives better overlapping with the C(2*sp*) atomic orbital and gives increased binding. The hybridization of the σ-bond-forming orbital of the X atom is of importance in partially explaining the decrease in r(CX) and the increase in f(CX) in going from the CH_3X series to the XCN series. The lone-pair electrons originally with configuration $Cl(3s)^2$ are now in a hybridized nonbonding orbital.

It is accepted that a measure of the strength of a bond is afforded by the overlap integral (59). McColl (52), considering carbon–hydrogen bonds, has shown that the overlap integral increases by 5.5 per cent when the carbon hybrid orbitals change from the sp^3 to the sp type. This change may be correlated with a change of 15 per cent in the force constant for the carbon–hydrogen bond. Considering the CX bond, then, it can be argued that since hybridization changes occur at the X atom also, a 15 per cent increase in f(CX) is expected to be a lower limit. In order to increase say f(CCl) by the extra 30 per cent necessary to bring it up to the figure found in ClCN, it is necessary to suppose that the overlap integral is increased by a further 10 per cent due to the hybridization of the chlorine atom. This seems reasonable, since there are grounds for believing that a change of sp ratio of some 2 per cent in the $3p_x$ atomic orbital of chlorine would be sufficient to increase the overlap integral by 10 per cent (23). Since the halogen–carbon bond length is decreased by this end-atom hybridization effect, it is possible that the small increases in r(CN) are brought about by van der Waals forces or repulsion between the end atoms.

It has been pointed out that in certain cases nuclear quadrupole coupling constants give direct information on the valence states of atoms in molecules (64). When nitrogen is triply bonded, as in the XCN series, the N^{14} coupling constant is about −4 Mc. per second (table 6). The molecules CH_3NC and NNO possess quadrivalent nitrogen atoms whose coupling constants are found to be very small.

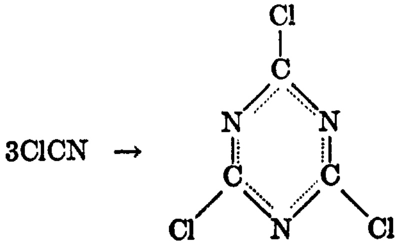
The hydrogen atom in hydrogen cyanide is to a certain extent acidic ($K = 10^{-9}$).

TABLE 7

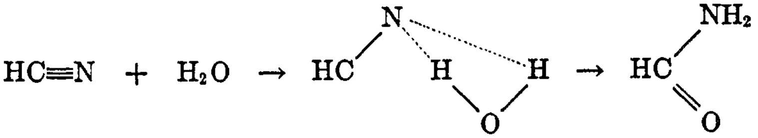
Molecular parameters for the NNO *molecules*

Bond	Bond Moment	Bond Length	Force Constant	Stretching Frequency	Bond Order
	D	*A.*	*10^5 dynes/cm.*	*cm.$^{-1}$*	
NN	0.50	1.126	17.88	2223.5	2.45
NO	0.67	1.191	11.39	1285.0	1.51
Reference	(87)	(11)	(72)	(70)	(60)

Nitriles polymerize and form addition compounds with other molecules, e.g.,



Here one of the π bonds in the CN group breaks and the singly occupied atomic orbitals on the carbon and nitrogen atoms pair up with similar atomic orbitals on adjoining nitrogen and carbon atoms, forming σ bonds. During the reaction



the two π bonds of the carbon–nitrogen link are broken and in the end product are replaced by two σ bonds to hydrogen.

L. Nitrous oxide; azide ion

The absorption spectrum of nitrous oxide vapor and the x-ray data (81) on solid and liquid nitrous oxide demonstrate conclusively the linearity of the molecule. The molecule is not, however, centrosymmetrical (70); it has the configuration N—N—O and a dipole moment of 0.17 D (82).

Examination of table 7 shows that the bonds of nitrous oxide are of hybrid character, with an excess π-bond order of ~1.5 in the nitrogen–nitrogen link and one of ~0.5 in the nitrogen–oxygen bond.

Since the molecule is linear the central nitrogen atom is *sp* hybridized. The molecule possesses sixteen valence electrons which are sufficient to fill the eight lowest-energy molecular orbitals detailed in Section VII,D.

The terminal nitrogen atom has associated with it three bonding molecular orbitals each containing two electrons; it possesses one σ bond and two π_D bonds; it is trivalent. The two π^* molecular orbitals are practically nonbonding, since the oxygen atom and the terminal nitrogen are relatively far apart. The terminal atoms each possess a lone pair of electrons situated in orbitals which are in all probability hybridized to some extent. We can expect then atomic dipoles at these atoms whose contributions to the total dipole moment of the molecule will tend to annul each other, since they are in opposition. Some evidence for this picture of "terminal" hybridization is afforded by the recent work of Mulliken (58), who has indicated that even in the homonuclear molecule N_2 the lone-pair orbitals possess some 14 per cent p character. The low value of the dipole moment indicates that the net effect of the atomic dipoles on the terminal atoms is largely to annul the polar effect of the NO group (*cf.* NO). The nitrogen atomic dipole has then a higher value than that associated with the oxygen atom. This affords a reasonable explanation of the low value found for the dipole moment of NNO, which is sensibly equal to that found for NO. All that seems to have happened is that the atomic dipole is not now adjacent to the nitrogen–oxygen bond as in nitric oxide but separated by the nitrogen–nitrogen bond.

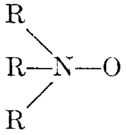
The bond-order values indicate that the electrons in the π_D bonds are not shared equally by the nitrogen–nitrogen and nitrogen–oxygen links, the probability of finding the π electrons in the vicinity of the nitrogen–nitrogen bond being considerably greater than that for the nitrogen–oxygen bond.

The azide ion is linear and isoelectronic with nitrous oxide and hence it will possess the same number and the same type of filled molecular orbitals. The nitrogen–nitrogen bonds are necessarily identical in this molecule, the density of the π electrons being the same for both links.

M. Amine hydrochlorides; amine oxides

The crystal structure of CH_3NH_3Cl has been determined (37); the carbon–nitrogen bond length is 1.47 ± 0.03 A. This gives a clear indication that the carbon–nitrogen bond is a pure σ bond and that the compound is best formulated as $(CH_3NH_3)^+Cl^-$; i.e., the nitrogen is sp^3 hybridized and quadrivalent.

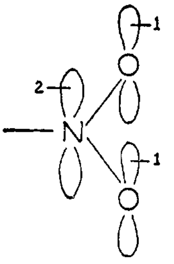
Amine oxides can be pictured symbolically as:



An electron diffraction study (47) has shown that the valence bonds are arranged tetrahedrally about the nitrogen atom and that the nitrogen–oxygen bond length is 1.36 A. This is a little shorter than the predicted theoretical value for the nitrogen–oxygen single bond. No firm conclusion can be drawn from this difference, since it is difficult to estimate the probable error of the electron diffraction measurement and the effect of the highly polar nature of the bond on its length. It seems clear, however, that the nitrogen atom utilizes four predominantly sp^3-type hybrids to form σ bonds with the three groups R and with the oxygen atom. The nitrogen–oxygen link is best described as a pure σ bond possessing considerable ionic character.

N. Nitro compounds

In nitro compounds, RNO_2, the RN and NO valence bonds are coplanar, the ONO angle being near 120° in value. The distribution of π-type electrons can be pictured as:



The experimental data on bond lengths and vibrational frequencies indicate that these π electrons are fed into a delocalized bonding and an $O \leftrightarrow O$ antibonding π^*-type molecular orbital. The former imparts a certain amount of double-bond character to the nitrogen–oxygen links; since the oxygen atoms are relatively far apart, the latter does not appreciably nullify the π-bonding effect. The nitrogen atom is quadrivalent: N(three σ, one π_D).

The information at present available for nitrogen–oxygen links does not permit the setting-up of a reliable relationship between bond order and bond length. Lüttke (49) has shown that a relationship exists between NO bond-stretching frequencies and bond length. This can be used to give an indication of the nitrogen–oxygen bond length (and hence its character) in those molecules where the NO frequencies have been assigned.

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