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Dimers of Nitrogen Dioxide. II. Structure and Bonding[1a,b]

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Received December 3, 1962

NO_2 can form two dimers, $O_2N–NO_2$ and $ONONO_2$. Each dimer can exist in several conformations. The current status of the spectroscopic evidence for these conformers is discussed and some suggestions are offered regarding their structures and the nature of the nitrogen–nitrogen bond in $O_2N–NO_2$. From a consideration of the Pauli principle and the occurrence of anticoincidence between spin-sets in the nitro group, it is concluded that the central bond in $O_2N–NO_2$ can perhaps be best described as a "splayed single bond." Vicinal interactions between unshared oxygen atom electrons and the nitrogen–nitrogen antibonding orbital in $O_2N–NO_2$ appear to be important. Together these factors provide an account for five curious features of $O_2N–NO_2$; *viz.*, its long N–N bond, its large ONO angle, its high barrier to internal rotation, its planarity, and its stability relative to the isomers $ONONO_2$ and ONOONO.

Introduction

In a previous report from this Laboratory[1b] it was suggested that nitrogen dioxide can under appropriate conditions dimerize to form three spectroscopically distinct dimers.

The dimer most stable under ordinary conditions has the planar $O_2N–NO_2$ structure in which the two nitro groups are linked together by a weak nitrogen–nitrogen bond. The bond lengths and bond angles in this dimer in the pure solid have been determined by X-ray diffraction by Broadley and Robertson.[2] The structure of the dimer in the gaseous state has been determined by electron diffraction by Smith and Hedberg.[3] Its infrared spectrum in the solid, liquid, and gaseous phases has been carefully examined by Snyder and Hisatsune.[4]

At liquid-nitrogen temperatures it appears that the dimer $O_2N–NO_2$ can be trapped in a twisted or skew, non-planar structure.[1b] Confirmation of the existence this structure has been obtained independently by Hisatsune, Devlin, and Wada.[5]

At liquid-helium temperatures it is possible to stabilize yet a third structure for the dimer. Its spectrum in some respects is very different from that of the previously mentioned conformers of the isomer $O_2N–NO_2$. It has been suggested that the dimer seen at liquid-helium temperatures has the structure $ONONO_2$.[1b]

It is the purpose of the present paper to discuss the current status of the spectroscopic evidence for the dimer $ONONO_2$ and to offer some new suggestions regarding the structure of this dimer and the nature of the nitrogen–nitrogen bond in the dimer $O_2N–NO_2$.

The experimental technique used in generating these dimers at liquid-helium temperatures and in obtaining their spectra and in making spectral assignments has been given in detail in part I.[1b]

The Dimer $ONONO_2$

Spectroscopic Data.—The nitro group of nitro compounds, $R–NO_2$, has three characteristic group frequencies: a nitrogen–oxygen asymmetric stretching frequency, usually around 1600–1700 cm.$^{-1}$; a nitrogen–oxygen symmetric stretching frequency, usually around 1300 cm.$^{-1}$; and an oxygen–nitrogen–oxygen bending frequency, usually around 750 cm.$^{-1}$. It has been found that the asymmetric stretching frequency correlates well with the electronegativity of the attached substituent, R.[1b] As the electronegativity of the attached substituent increases, the asymmetric frequency steadily increases. When the substituent is a fluorine atom the asymmetric stretching frequency has its highest reported value (exceptingt hat for the nitronium ion), 1793 cm.$^{-1}$. Yet with carefully purified NO_2 deposited in an argon matrix at liquid-helium temperatures there is found an intense absorption at 1829 cm.$^{-1}$. This is well above the region of the nitro-group's asymmetric stretching frequency. Evidently there exists in the deposited sample a polar bond whose bond order is greater than the bond order of the nitrogen–oxygen bond in the nitro group. In fact, the spectroscopic features of such deposits fit well the features expected for a molecule that contains both a nitroso group and a nitro group.

The original assignment of the observed spectrum to the dimer $ONONO_2$ was based upon these considerations and upon the further fact that the spectrum under consideration was very similar to that of dinitrogen trioxide,[1b,5,6] which in its stable form, $ONNO_2$ (not ONONO), also contains both a nitroso and a nitro vibrational functional group (Fig. 1).

Recently Dr. Robert St. Louis in these Laboratories has improved the technique of producing $ONONO_2$. This has made it possible for him to locate and to assign to this molecule three new bands, bringing the total of the observed bands for this species to seven. On gently warming a sample containing $ONONO_2$, he

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[1] (a) Presented at the Symposium on the Chemistry of Group V Elements at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 9–14, 1962; (b) Part I: W. G. Fateley, H. A. Bent, and B. Crawford, Jr., *J. Chem. Phys.*, **31**, 204 (1959).

[2] J. S. Broadley and J. M. Robertson, *Nature*, **164**, 915 (1949).

[3] D. W. Smith and K. Hedberg, *J. Chem. Phys.*, **25**, 1282 (1956).

[4] R. G. Snyder and I. C. Hisatsune, *J. Mol. Spectry.*, **1**, 139 (1957).

[5] I. C. Hisatsune, J. P. Devlin, and Y. Wada, *J. Chem. Phys.*, **33**, 714 (1960).

[6] L. D'Or and P. Tarte, *Bull. soc. roy. Liège*, **22**, 276 (1953).

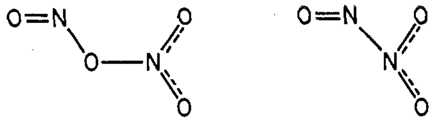

Fig. 1.—Structures of $ONONO_2$ and $ONNO_2$.

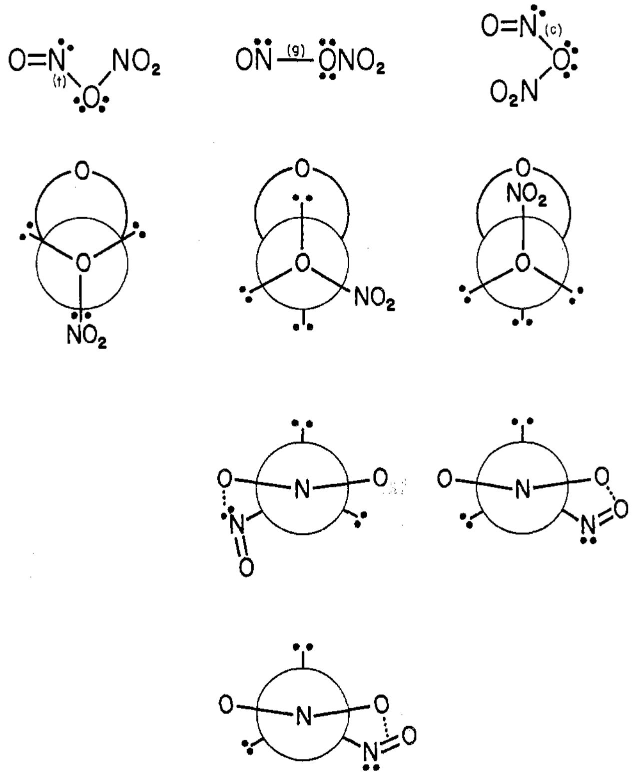

Fig. 2.—Possible confomers of $ONONO_2$.

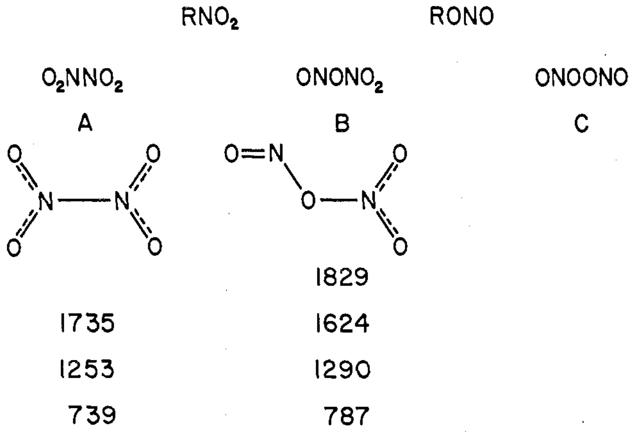

Fig. 3.—Summary of spectroscopic evidence on the dimers of NO_2.

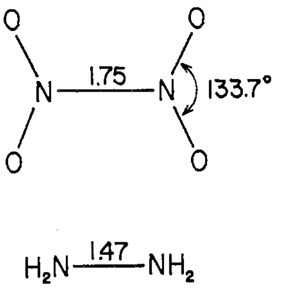

Fig. 4.—Structure of O_2N-NO_2.[3]

has found that these seven bands disappear and reappear in slightly shifted positions. This strongly suggests that in a solid matrix the dimer $ONONO_2$ can exist in several conformations.

Structure.—With respect to the (nitroso nitrogen)–(interior oxygen) single bond, ON–ONO_3, the nitroso group and the nitro group could be with respect to each other either *trans*, *gauche*, or *cis*. These conformers as seen in projection along the ON–ONO_3 nitrogen–oxygen single bond are shown in the three diagrams immediately beneath the structural formulas in Fig. 2. In these diagrams the curved lines to the uppermost oxygen atom represent the the equivalent orbital components[7] of the nitrogen–oxygen double bond of the nitroso group.

In the *trans* conformer the electrons of the nitroso double bond and the lone pair on the nitroso nitrogen atom are in an essentially eclipsed position with respect to the lone pairs on the interior oxygen atom and the bond ONO–NO_2 between this oxygen atom and the nitro group. The *trans* conformer is therefore probably two to three kilocalories per mole less stable than conformers based upon the *gauche* and *cis* configurations in which, as shown, these electron pairs are staggered with respect to each other. The problem of predicting the relative stability of the *trans* conformer is analogous to the problem of predicting the equilibrium conformation of a methyl group adjacent to a double bond. The solution to this problem for acetaldehyde has been obtained experimentally by Kilb, Lin, and Wilson[8] and for propylene by Lide and Mann[9] and has been discussed in more general terms by Pauling.[10]

Possible orientations of the nitro group with respect to the remainder of the molecule for the previously cited *gauche* and *cis* conformers are shown in the bottom three projections in Fig. 2. These are projections along the ONO–NO_2 bond, the (nitro nitrogen)–(interior oxygen) single bond.

In no case does it seem possible to find a reasonable orientation of the nitro group that leaves the lone pairs on its oxygen atoms completely free from unfavorable steric interactions with some part of the nitroso group (the dotted lines in Fig. 2). For the *gauche* conformer, the nitro group's oxygen atom lone pairs interfere with either the lone pair on the nitroso nitrogen atom or with one of the components of the nitroso group's double bond. In the *cis* conformer the nitro group interferes with one of the lone pairs on the nitroso group's oxygen atom. At the present time it does not seem possible to assay even qualitative guesses as to the relative stabilities of these structures.

Structural Forms of N_2O_4.—Nitrogen dioxide can add to alkyl radicals through either its nitrogen atom to form organic nitro compounds or through one of its

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(7) J. A. Pople, *Quart. Rev.* (London), **11**, 273 (1957).

(8) R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., *J. Chem Phys.*, **26**, 1695 (1957).

(9) D. R. Lide, Jr., and D. E. Mann, *ibid.*, **27**, 868 (1957).

(10) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, pp. 140–142.

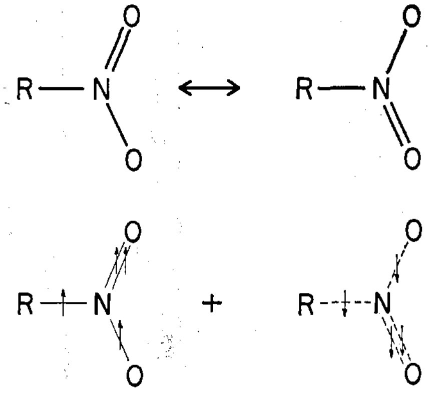

Fig. 5.—Electron correlation in the nitro group. Top row: classical spin-paired resonance structures. Each line represents a pair of electrons. Bottom row: partially anticoincident configuration of the two spin-sets. Each line (solid or dashed) represents one electron.

oxygen atoms to form organic nitrites. Therefore it is perhaps not surprising to find that it can add to itself to form the analogous structures A and B, respectively (Fig. 3).

While isomer A is more stable than isomer B, the latter is nonetheless of considerable chemical interest. Homolytic scission of the bond ON–ONO$_2$, for example, would yield the radicals NO and NO$_3$; as recently discussed by Powell,[11] it is the presence of the latter radical, NO$_3$, that is chiefly responsible for the reactivity of "N$_2$O$_4$" in the gas phase. On the other hand, heterolytic scission of the same bond would yield the ions NO$^+$ and NO$_3^-$; as Addison[12] has shown, this accounts for many of the chemical properties of "N$_2$O$_4$" in condensed phases.

Both isomers A and B can evidently exist in several conformations. The assignment of structures to these conformers is more certain for isomer A than it is for isomer B and it is with isomer A that the remainder of this paper is concerned.

The Dimer O$_2$N–NO$_2$

Anomalous Features.—The structure of the dimer O$_2$N–NO$_2$ in the gas phase as determined by Smith and Hedberg[3] is given in Fig. 4. This structure is anomalous in five respects.

First, the nitrogen–nitrogen bond is unusually long, almost 0.3 Å. longer than the corresponding bond in hydrazine, for example. Second, the ONO angle is unusually large; the OSO angle in sulfuryl fluoride, for example, is 124°. Third, the molecule is planar; *i.e.*, the substituents on the nitrogen atoms—the oxygen atoms—are eclipsed with respect to each other rather than staggered. Fourth, the barrier to rotation about the nitrogen–nitrogen bond is unusually large for so long a bond; Snyder and Hisatsune[4] have estimated that the barrier in O$_2$N–NO$_2$ is nearly as large as that in ethane. Fifth, the molecule, even despite the presence of adjacent identical formal charges on the nitrogen atoms, is relatively stable, more stable, for example, than either the isomer ONONO$_2$ or the isomer ONOONO.

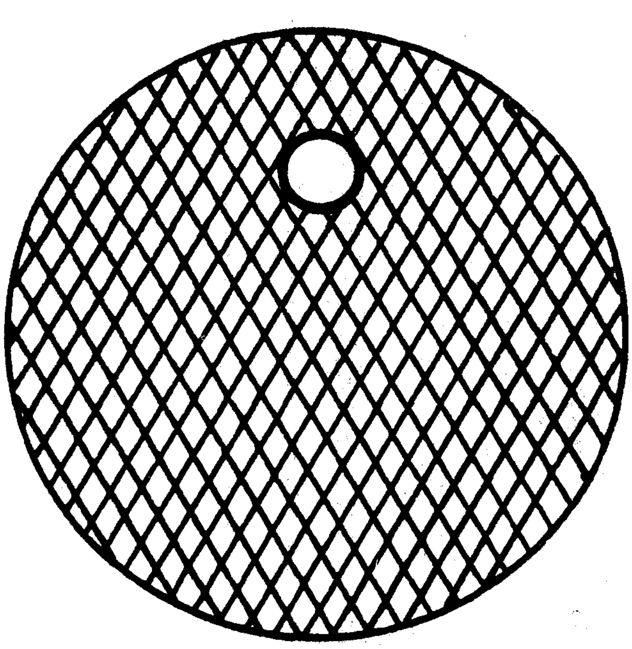

Fig. 6.—Fermi hole.

To summarize, the following facts about O$_2$N–NO$_2$ need to be explained: (1) long N–N bond; (2) large ONO angle; (3) planarity; (4) high barrier; and (5) relative stability.

Previous discussions of the electronic structure of the ground state of O$_2$N–NO$_2$ have generally been primarily concerned with explaining the planarity of the molecule and the barrier to rotation (items 3 and 4). Attention has been focused upon the nature of the nitrogen–nitrogen bond, which has been described as a "π-only" bond. This idea, first mentioned by Smith and Hedberg,[3] has been elaborated upon by Coulson and Duchesne,[13] but has been criticized by Pauling,[14] Green and Linnett,[15] and Brown and Harcourt,[16] who consider the bond to be more nearly a σ-bond. It will be suggested here that considerations of the nature of electron correlation in molecules imply that the nitrogen–nitrogen bond in O$_2$N–NO$_2$ may perhaps be best described as a "splayed single bond."

Electron Correlation in the Nitro Group.—The nitro group, like the carboxyl group with which it is isoelectronic, can be represented by two classical valence-bond structures (Fig. 5). It is traditional in such cases as this to say that the structure is stabilized by "resonance" or, alternatively, by "electron delocalization." Recently Linnett[17] has suggested an alternative interpretation. This interpretion focuses attention upon

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(11) R. E. Powell, Symposium on the Chemistry of Group V Elements, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 9–14, 1962.

(12) C. C. Addison, *Angew. Chem.*, **72**, 193 (1960); also, Symposium on the Group V Elements, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 9–14, 1962.

(13) C. A. Coulson and J. Duchesne, *Bull. Classe Sci., Acad. roy. Belg.*, **43**, 522 (1957).

(14) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, pp. 350–351.

(15) M. Green and J. W. Linnett, *Trans. Faraday Soc.*, **57**, 10 (1961).

(16) R. D. Brown and R. D. Harcourt, *Proc. Chem. Soc.* (London), 216 (1961).

(17) J. W. Linnett, *J. Am. Chem. Soc.*, **83**, 2643 (1961).

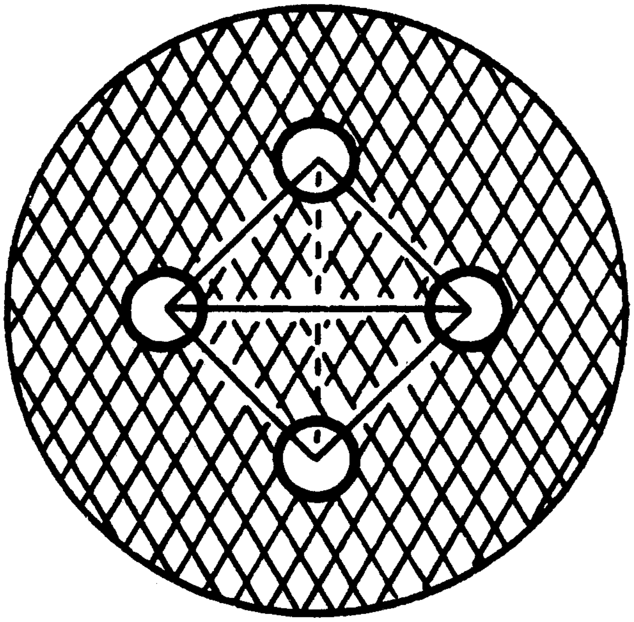

Fig. 7.—Configuration of maximum probability for four valence-shell electrons of parallel spin. The atomic core is located at the center of the tetrahedron.

two factors that produce to some degree correlation in the motions of the electrons in molecular systems.

One factor—it is perhaps the most important one—is the Pauli principle, which states that the wave function Ψ must be antisymmetric with respect to an interchange in the coördinates of any two electrons. For example, for the interchange of coördinates (spatial and spin) of electrons 1 and 2, the Pauli principle states that

$$\Psi(x_1, x_2, x_3, \ldots) = -\Psi(x_2, x_1, x_3, \ldots) \qquad (1)$$

In this expression, $x_i = r_i,\zeta_i$, where r_i represents the spatial coördinates of electron i (say its cartesian coördinates x_i, y_i, z_i) and ζ_i represents its spin coördinate. A consequence of eq. 1 is that the wave function must vanish whenever electrons 1 and 2 have the same coördinates (spatial *and* spin). For example, if x_1 and x_2 are equal to some common value, x, it follows from (1) that

$$\Psi(x, x, x_3, \ldots) = -\Psi(x, x, x_3, \ldots)$$

and, hence, that

$$\Psi(x, x, x_3, \ldots) = 0 \qquad (2)$$

Frequently this result is expressed by saying that "two electrons with parallel spins cannot be in the same place at the same time."

The Pauli principle does not say that the wave function must vanish when $r_1 = r_2$ if the two electrons have opposite spins; for then $\zeta_1 \neq \zeta_2$ and $x_1 \neq x_2$.

The physical significance of the statement summarized in eq. 2 is illustrated in Fig. 6. About each electron of given spin exists an excluded volume or as Slater has called it a "Fermi hole" consisting of a deficiency of charge of the same spin as the electron in question.[18] A figure such as this was suggested first in 1933 by Wigner and Seitz in a discussion of the electronic structure of sodium metal.[19] The area cross-hatched in Fig. 6 represents the electron cloud of a many-electron system. The small circle represents the location of a specific electron within whose near-neighborhood the probability of finding another electron of the same spin is very small.

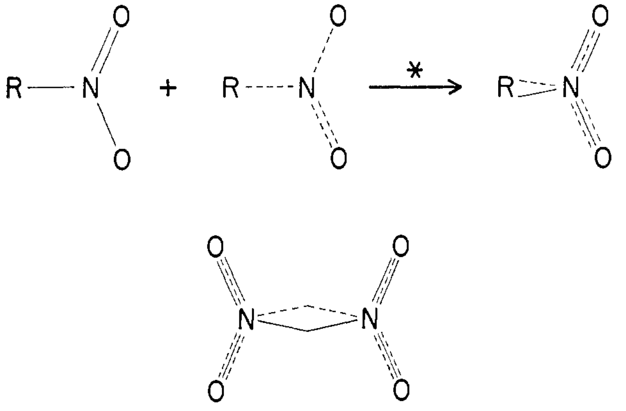

Fig. 8.—Electronic structure of the nitro group and of the dimer O_2N–NO_2. First line: spin-set superposition showing anticoincidence of the two spin orbitals that project from the nitrogen atom of a nitro group. Second line: overlap of anticoincident spin orbitals to produce a splayed bond.

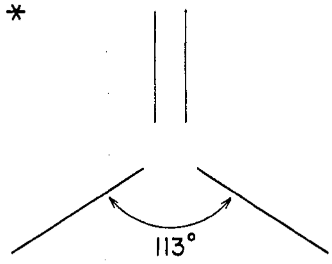

Fig. 9.—Typical valence angle opposite a double bond.

A question of considerable chemical interest concerns the nature of the most probable configuration of the centers of the Fermi holes of the four electrons of parallel spin that are present in the valence shell of a first-row element which in its chemical union satisfies the octet rule. It has been argued by several authors,[20–22] and is in any event perhaps chemically obvious, that the configuration of maximum probability for four such electrons is essentially that shown in Fig. 7. Figure 7 shows that if the valence shell of an atom contains four electrons whose spins are parallel, the electrons will tend to be disposed with respect to each other as are the corners of a regular tetrahedron. The four electrons of opposite spin that complete the atom's octet will be similarly disposed with respect to each other and the atomic core. The orientation of the first spin-set with respect to the second will then depend largely upon classical electrostatic forces. This is the second factor that introduces correlation in the motions of the electrons in a molecular system.

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[18] J. C. Slater, *Phys. Rev.*, **81**, 385 (1951).

[19] E. Wigner and F. Seitz, *ibid.*, **43**, 804 (1933); *ibid.*, **46**, 509 (1934).

[20] H. K. Zimmerman, Jr., and P. Van Rysselberghe, *J. Chem. Phys.*, **17**, 598 (1949).

[21] J. W. Linnett and A. J. Poe, *Trans. Faraday Soc.*, **47**, 1033 (1951).

[22] C. E. Mellish and J. W. Linnett, *ibid.*, **50**, 657, 665 (1954).

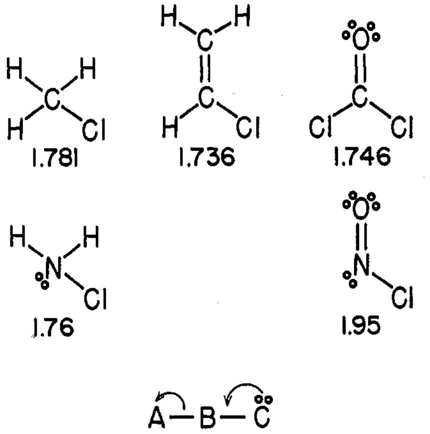
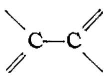


Fig. 10.—Examples of bond lengthening by vicinally located unshared electrons.[32]

Generally speaking the two spin-sets about a combined atom will be largely coincident if there are two or more chemical bonds to the atom. But as Linnett has emphasized,[17] this need not always be the case. In fact, in the nitro group the electrons in one spin-set may assume the orientation implied by say the first valence-bond structure in Fig. 5, while those in the second spin-set can adopt the orientation implied by the second valence-bond structure. This possibility is shown diagrammatically in the bottom half of Fig. 5. Each solid or dashed line in the bottom two structures in Fig. 5 represents *one* electron, not a pair. By adopting these partially anticoincident configurations, $e(\uparrow)-e(\downarrow)$ repulsions are diminished from what they would be in the conventional spin-paired structures. The actual molecule is then to be viewed as a superposition of these two diagrams (Fig. 8).

However, in the superposition of the two separate spin-set structures of the nitro group it is important to recall that the normal valence angle opposite a double bond is not usually, if ever, 120°. A more typical value is 113° (Fig. 9). Thus it is to be expected that the two spin orbitals that project from the nitrogen atom of a nitro group will not be exactly coincident, although precisely to what degree they are anticoincident it does not at the present time seem possible to say. The important qualitative point, however, is that in order for these orbitals to overlap well with the two spin orbitals that project from the nitrogen atom of a second nitro group it is necessary for the atoms of both nitro groups to lie in a common plane. The nitrogen–nitrogen bond that is formed in this way is illustrated at the bottom of Fig. 9. It may be described as a splayed single bond.

In this way both the planarity of the dimer and the barrier to rotation about its central bond are accounted for. Its stability relative to the dimers $ONONO_2$ and ONOONO probably arises from the fact that the dimer O_2N-NO_2 contains two nitro groups. $ONONO_2$ contains only one nitro group and ONOONO contains none. Hence, of the three dimers, O_2N-NO_2 is the dimer that best allows for the development of anticoincidence between the two spin-sets of the dimer's electron cloud.



Cycloöctatetraene	1.46
Butadiene	1.48
2,2′-Bipyridine	1.50
Oxalate ion	1.54

Fig. 11.—Further examples of bond lengthening by vicinally located unshared electrons.

Not explained by this discussion is the long N–N bond and the large ONO angle.

Bond Lengthening by Unshared Electrons.—The length of the nitrogen–nitrogen bond in O_2N-NO_2 is unusual from two standpoints. First, it is now generally recognized that a change in atom hybridization often is accompanied by a marked change in bond lengths.[23–30] As a rule bond lengths decrease as the s content of the corresponding hybrid orbitals increases. For a carbon–carbon single bond a change in hybridization of one of the participating carbon atoms from sp^3 to sp^2 or from sp^2 to sp generally corresponds to a shortening of the corresponding bond by 0.03–0.04 Å. Since the nitrogen atom of a nitro group is described as sp^2 hybridized whereas the hybridization of the nitrogen atoms in hydrazine is sp^3, one might have supposed by analogy with carbon–carbon bonds that the nitrogen–nitrogen bond in O_2N-NO_2 would be 0.06–0.08 Å. shorter than the nitrogen–nitrogen bond in hydrazine rather than 0.28 Å. longer. And second, it has been found that bonds in the vicinity of electronegative atoms are often shorter than normal.[27,31] Hence in going from hydrogen (in hydrazine) to oxygen (in O_2N-NO_2) as the substituent on nitrogen one might have expected, again, a shortened bond.

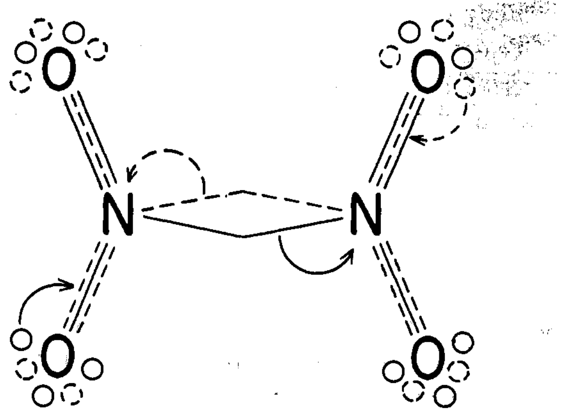


Fig. 12.—Vicinal interactions between oxygen atom unshared electrons and the nitrogen–nitrogen antibonding orbital in O_2N-NO_2.

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(23) M. G. Brown, *Trans. Faraday Soc.*, **55**, 694 (1959).
(24) C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.*, **30**, 777 (1959).
(25) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959); *ibid.*, **11**, 96 (1960).
(26) G. R. Somayajulu, *J. Chem. Phys.*, **31**, 919 (1959).
(27) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).
(28) O. Bastiansen and P. N. Skancke, *Advan. Chem. Phys.*, **3**, 323 (1961).
(29) O. Bastiansen and M. Traetteberg, *Tetrahedron*, **17**, 147 (1962).
(30) D. R. Lide, Jr., *ibid.*, **17**, 125 (1962).
(31) H. A. Bent, *J. Chem. Phys.*, **33**, 1260 (1960).

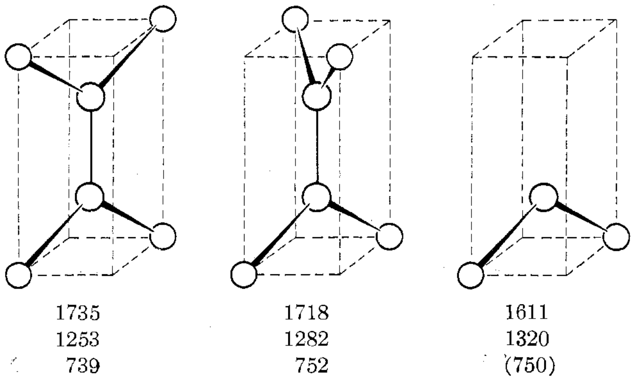


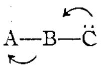
Fig. 13.—Group frequencies of the nitro group in planar and non-planar $O_2N\text{–}NO_2$ and in free NO_2. Asymmetric and symmetric N–O stretching frequencies and ONO bending frequency, respectively.

There is one sense, however, in which the length of the nitrogen–nitrogen bond in $O_2N\text{–}NO_2$ fits into an established pattern. In a structure $A\text{–}B\text{–}\ddot{C}$ (the bonds between A and B and between B and C need not be single bonds) bond A–B may sometimes be abnormally long when atom C has on it unshared electrons, particularly if the anion A^- is a relatively weak base. The length of the carbon–chlorine bond in acetyl chloride (A = chlorine, B = carbon, C = carbonyl oxygen), for example, is longer than the length of the same bond in vinyl chloride (C = methylene group) (Fig. 10). Additional examples have been summarized elsewhere.[32] Particularly to the point is the trend in carbon–carbon single bond lengths shown in Fig. 11. This series terminates with the oxalate ion, which is isoelectronic with $O_2N\text{–}NO_2$.

Often (though not always) these bond-lengthening effects can be attributed to the interaction of unshared electrons on atom C with the interior lobe of the antibonding orbital associated with the vicinally located bond A–B. Broadly speaking this interaction corresponds to the well known structural diagrams that are used to represent departures from perfect pairing.[33]

$$A\text{–}B\text{–}\ddot{C} \longleftrightarrow A{:}^-\ B{=}C^+$$

or



$$A\text{—}B\text{—}\ddot{C}$$

Such an interaction represents a further method for developing anticoincidence between spin-sets. Its application to the dimer $O_2N\text{–}NO_2$ is illustrated in Fig. 12.

In this way the abnormal length of the nitrogen–nitrogen bond is qualitatively accounted for. In addition there is obtained an explanation for the relatively large ONO angle. For in the dimer $O_2N\text{–}NO_2$ there is as suggested by the work of Linnett[17] and Green and Linnett[34] one spin-set about each nitrogen atom (on the left in Fig. 12 the spin-set represented by the solid lines; on the right the spin-set represented by the dashed lines) that tends toward a configuration characteristic of the electrons about an atom flanked by two double bonds, such as in CO_2 or NO_2^+, which are linear molecules.

Concluding Remarks.—A further implication of the present description of the nitrogen–nitrogen bond in $O_2N\text{–}NO_2$ concerns the changes that occur in the properties of this dimer as the nitro groups are rotated about the central bond from an eclipsed to a staggered configuration. According to the present view a rotation of this kind should diminish the orbital overlap in the nitrogen–nitrogen bonding region and therefore should tend to destabilize the molecule, as observed, and should tend to make the two nitro groups approach more closely than before the character of the free NO_2 monomer. As illustrated in Fig. 13, there is indeed a steady decrease in the asymmetric stretching frequency and, correspondingly, a steady increase in the symmetric stretching frequency in going from planar $O_2N\text{–}NO_2$ through twisted $O_2N\text{–}NO_2$ to free NO_2. At the present time there is no direct evidence regarding the change in length of the bond between the two nitrogen atoms. One would expect the bond to become longer. In the isoelectronic oxalate ion $^-O_2C\text{–}CO_2^-$ an internal rotation of the kind described increases the length of the central bond approximately 0.02 Å.

Acknowledgments.—This study was supported by a grant from the Graduate School of the University of Minnesota of a Faculty Summer Research Appointment and by a du Pont Grant-in-aid to the Department of Chemistry of the University of Minnesota. This support is gratefully acknowledged.

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(32) H. A. Bent, *J. Chem. Phys.*, **36**, 1090 (1962).

(33) Because the energy of an antibonding orbital decreases as the length of the corresponding bond increases, interaction of unshared electrons on atom C with the antibonding orbital $(A\text{–}B)^*$ will in general be favored by a long bond A–B. The interaction will be favored, also, from the standpoint of overlap, if (in the l.c.a.o. approximation) the coefficient of atom B's contribution to the antibonding orbital is as large as possible. Owing to the mutual orthogonality of the bonding and antibonding orbitals, this implies that the interaction will be favored if the coefficient of atom A's contribution to the bonding orbital is large; *i.e.*, if the bond A–B is polar in the sense A^-B^+.

(34) M. Green and J. W. Linnett, *J. Chem. Soc.*, 4959 (1960).