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STRUCTURE AND PROPERTIES OF NITROSO COMPOUNDS

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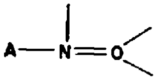
Abstract—The electronic structure of organic compounds containing NO bonds has been considered in relation to their observed lengths and characteristic frequencies. The relation between these properties and "bond-order" has been examined for a number of molecules and ions for which the electronic structures are well defined. These relationships are then used for the discussion of other compounds for which the electronic structures are less certain. It has been shown that many of the molecules contain bonds of non-integral order; structures in which the NO bonds contain an odd number of electrons have been proposed in certain cases, the double-quartet hypothesis being used to describe the electron distribution. It has been shown that the pattern of bond lengths and characteristic frequencies can then be understood, as well as such unexplained observations as the dimerization of alkyl nitroso-compounds and the non-existence of dimers of nitrosyl halides.

INTRODUCTION

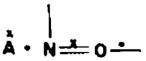
Compounds containing the nitroso group show an interesting variety of properties. For instance, some nitroso-compounds, ANO, in which A is a monovalent atom or radical dimerize while others do not; also the N—O bond length and group vibration frequency are variable; further the AN bond has sometimes an unexpected length. It is the purpose of this paper to consider the electronic structures of these compounds, and to attempt to offer an explanation of the considerable differences in some observed properties.

Structures of nitroso-compounds

As has been suggested elsewhere, two covalent structures are possible for ANO. They are I and II, where the lines represent pairs of electrons, and crosses (x) single



I



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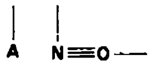

III

electrons having one spin, and circles (o) those having the other. (Dots will be used for single electrons when the spin is not specified.) In each of these, the separate atoms have valence shells which are octets (or a pair if A is hydrogen). The ionic formula III also provides satisfactory electron shells and may be a small contributor to a resonance hybrid if a more precise description of the structure is required. However the contribution is likely to be small for the ground state because it involves a considerable charge separation (formal charges on the three atoms: -1, 0 and $+1$). Of the covalent structures, I possesses the satisfactory feature that it places a zero formal charge on each atom, whereas the formal charge distribution for II is $-\frac{1}{2}$, 0,

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$+\frac{1}{2}$. On the other hand I contains six electron pairs in the same bond or in the same lone-pair orbital; this increases the inter-electron repulsion energy. But in II the electrons of one spin occupy different spatial orbitals from those of the other spin, thus reducing inter-electron repulsion. Hence II will be favoured if A is an atom or group capable of assuming readily a formal charge of $-\frac{1}{2}$, while I will be favoured if it is not. Thus if A is a halogen atom it might be expected that II would be favoured for the ground state, whereas if A is an organic radical such as methyl or phenyl it would be anticipated that I would be the structure. That this conclusion is, in general, justified is borne out by the bond length and IR data. For nitrosyl halides[1]: BrNO: NBr, 2·14A; NO, 1·15 (cf. 1·15 in NO, but 1·06 in NO$^+$ and 1·21 in NHO); ClNO: NCl, 1·95 (1·76 in NHCl$_2$ and 1·77 in NH$_2$Cl), NO, 1·14; FNO: NF, 1·52; (cf. 1·37 in NF$_3$, 1·44 in FN=NF, and 1·35 in FNO$_2$) NO, 1·13A. Also the NO vibration frequency in NOCl and NOBr falls near 1800 cm^{-1}.[2] On the other hand those of the monomers of CH$_3$NO and C$_6$H$_{11}$NO are 1564 and 1558 cm^{-1} respectively,[2] (i.e. the force constant is probably about 25% smaller). In aromatic nitroso compounds the frequency of the monomer is about 1500 cm^{-1}.[2] These figures therefore confirm the broad trend though there may be special smaller variations to be considered. For instance, the NO vibration frequency in CCl$_3$NO is 1620 cm^{-1}.[2] which might be an electronegativity effect or it might suggest that some contribution from structures like II is favoured by the presence of the chlorine atoms with their unoccupied 3d orbitals (the frequency in CF$_3$NO is lower, 1595). However, our concern here is more with the considerable differences rather than with the smaller ones.

Pauling[3] explained the long nitrogen–halogen bonds in FNO, ClNO and BrNO by the proposal that the electronic structure is a resonance hybrid of I and III. The present hypothesis has two advantages over this. It requires that the NO bond lengths in FNO, ClNO and BrNO should *all* be equal to that in nitric oxide itself, which they are within the limits of experimental error. Secondly, according to Pauling's resonance hypothesis[3] it would be expected that the relative proportions of I and III contributing to the hybrid would change considerably in the series FNO, ClNO, BrNO, because of the changing electro-negativity of the halogen atom. That the change in electronic structure in the series is quite small is shown by the constancy of the NO bond lengths, and also by the relative constancy of the NO characteristic frequencies: FNO, 1844 cm^{-1}; ClNO, 1801; BrNO, 1799. The use of formula II and the hypothesis that this is the major contributing structure in all these compounds explains these structural facts naturally and easily.

A further difference from the resonace explanation is that the "driving force" for a molecule to assume II rather than I (which has zero formal charges throughout) is the *reduction of inter-electron repulsion.* Whereas I has six pairs of electrons occupying the same bond or lone-pair orbitals, II has none. It is supposed that, if other factors were unimportant, the energy of the system would be lower if the halogen atom had a zero formal charge. However in the nitrosyl halides, the reduction of inter-electron repulsion achieved by adopting II outweighs this.

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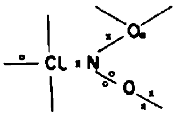
[1] L. E. Sutton. *Tables of Interatomic Distances, Chem. Soc. Special. Publ.* No. 11 (1958).

[2] L. J. Bellamy, *Infrared Spectra of Complex Molecules* (2nd Edition) p. 304. Methuen. London (1958).

[3] L. Pauling, *Nature of the Chemical Bond* (3rd Edition) p. 345. Cornell University Press, Ithaca (1960).

The structure of $ClNO_2$ illustrates this effect. The following structures may be regarded as possible ones. Of these, both place a formal charge of +1 on the nitrogen



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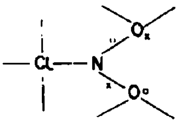
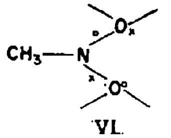


V

atom, and $-\frac{1}{2}$ on one of the oxygen atoms. Structure IV places the other $-\frac{1}{2}$ on the chlorine atom while V places it on the second oxygen atoms leaving the chlorine atom with a zero formal charge. Structure IV has no electron pairs occupying the same spatial region, whereas V has one (in the NCl bond). Electron repulsion therefore favours IV a little. This structure, however, has the unsatisfactory feature that the electrons of one spin favour ONO being linear while those of the other spin favour it being bent. With structure V, the electrons of each spin favour essentially the same shape. Therefore electron repulsion favours IV slightly, while the advantage of maintaining the spin-quartets round each atom as nearly as possible at the corners of a regular tetrahedron favours V (though it must be remembered that the bending force constants in systems containing —C≡ are small). Consequently we may expect IV and V to have approximately equal importance. The most recent data show that the NCl bond length is 1·840 ± 0·002,[4] which is intermediate between that of the single bond in NH_2Cl (1·77 A) and that of the one-electron bond in ClNO (1·95 A). The ONO angle is 130° 35′ ± 15′, which is larger than would be expected for V. This can be accounted for, because, in IV, the electrons of one spin favour the ONO being linear. There is a slight indication that the NO bond length in nitromethane (VI) is a little longer (1·22 ± 0·02 A) as would be expected and the ONO angle a little smaller (127 ± 4°) as would be expected. The angle of 130½ may be compared with that of 134·1° in NO_2 (VII) in which there are no "coincident" pairs, and the electrons of one spin (x) favours a linear molecule and those of the other spin (o) favour a bent molecule. The angle in this molecule is therefore naturally a little bigger than that in $ClNO_2$.



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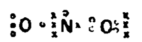
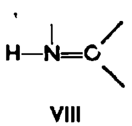


VII



VIII

The molecule HNO

This is known spectroscopically and has a lifetime of 1/10 second.[5] Because the hydrogen atom does not readily assume a negative charge the arguments of the last section would give it the structure VIII. The vibration frequencies for HNO are 3596, 1562 and 1110 cm^{-1}.[6,7] The first indicates that the NH bond is a normal single bond (cf. 3336 and 3414 cm^{-1} in NH_3). The second is very close to the NO frequency

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[4] D. J. Millen and K. M. Sinnott, *J. Chem. Soc.* 350 (1958).

[5] F. W. Dalby, *Canad. J. Phys.* **36**, 1336 (1958).

[6] K. B. Harvey and H. W. Brown, *J. Chim. Phys.* **56**, 745 (1959).

[7] J. K. Cashion and J. C. Polanyi, *J. Chem. Phys.* **30**, 316 (1959).

in CH_3NO (1564 cm^{-1}) and in $C_6H_{11}NO$ (1558 cm^{-1}), in which the structure[5] is undoubtedly I. The frequencies of DNO (2680, 1550 and 820 cm^{-1}) are consistent with the above. The NO bond length is 1·21 A[6] (cf. 1·15 in NO). On the other hand the NH bond length is 1·063 which is unexpectedly long compared with 1·015 in NH_3. This is rather reminiscent of the long bonds in Cl NO and Br NO though the percentage increase is very much smaller. Therefore most of the evidence favours VIII. The H—NO bond dissociation energy is 45–50 kcals/gm mol.[7,8] This small value must be due to the greater strength of the NO bond in NO compared with that in HNO.

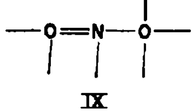
NO *stretching frequency and bond order*

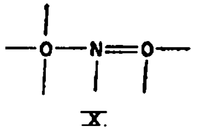
There are enough compounds for which the NO bond order is known with reasonable precision and certainty, and for which the NO stretching frequencies are also available, to determine whether a correlation between these two quantities exists which might be used to predict and assess bond order in molecules for which the electronic structure is uncertain.

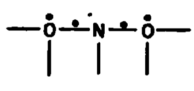
Nitric oxide itself has a bond order of 2½ whether considered from the point of view of molecular orbital theory,[9] Pauling's three-electron bond,[10] or double quartet[11] (or non-pairing) theory. The NO stretching frequency in this molecule is at 1876 cm^{-1}.[12] The loss of an electron from NO leaves the ion NO^+, isoelectronic with N_2, which undoubtedly contains a triple bond. Its NO stretching frequency falls in the range 2240–2340 cm^{-1}.[13] A number of the excited states of NO also have an effective bond order of three and their stretching frequencies lie in the range 2280–2340 cm^{-1}.[14]

For the NO double bond, the characteristic frequency in NHO will be taken (1562 cm^{-1}) together with those in CH_3NO (1564 cm^{-1}) and in $C_6H_{11}NO$ (1558 cm^{-1}).[15] The frequencies of aromatic nitroso compounds are a little lower (1488–1513 cm^{-1}). Robson and Tedder[16] have shown recently that the nitroso-acetylenes show frequencies of 1560–1580 cm^{-1} in solution at low temperatures where monomers are stable.

The nitrite ion, which is represented by Pauling[10] as a hybrid of IX and X, would be given the formula XI on the double quartet hypothesis, this last formula is supported


IX


X


XI

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[8] M. J. Y. Clement and D. A. Ramsay, *Canad. J. Phys.* **39**, 205 (1961).

[9] C. A. Coulson, *Valence*, p. 102. Oxford Univ. Press. London (1952).

[10] L. Pauling, *loc. cit.*, p. 343.

[11] J. W. Linnett, *Nature, Lond.* **187**, 859 (1960); *J. Amer. Chem. Soc.* **83**, 2643 (1961).

[12] E. L. Saier and A. Pozetsky, *Analyt. Chem.* **126**, 1079 (1954).

[13] D. J. Millen and D. Watson, *J. Chem. Soc.* 369 (1951); W. R. Angus and A. H. Leckie, *Proc. Roy. Soc.* A **149**, 327 (1935); H. Gerding and H. Houtgraaf, *Rec. Trav. Chim. Pays. Bas* **72**, 21 (1953).

[14] G. Herzberg, *Spectra of Diatomic Molecules* p. 558. Van Nostrand, Princeton, N.J. (1950).

[15] W. Luttke, *J. Phys. Radium* **15**, 633 (1954); *Z. Elektrochemie* **61**, 302 (1957); P. Tarte, *Bull, Soc. Chim. Belge* **63**, 525 (1954); J. Mason and J. Dunderdale, *J. Chem. Soc.* 754 (1956).

[16] E. Robson and J. M. Tedder, *Proc. Chem. Soc.* 13 (1963).

by calculations.[17] The bond order is 1½. The average of the symmetric and asymmetric stretching frequencies of this ion is 1285 cm^{-1}.[18] The average of the same two frequencies for nitromethane is 1465 cm^{-1}.[2] On the double-quartet hypothesis the formula is VI. According to this (and with resonance also) the bond order is 1½. The $^2\Pi_r$ excited state of nitric oxide is also believed to possess a bond of order 1½.[19] The frequency of 1022 cm^{-1} is included in Fig. 1. The range of frequencies for bonds of order 1½ is apparently much greater than for bonds of order 3, 2 and 1.

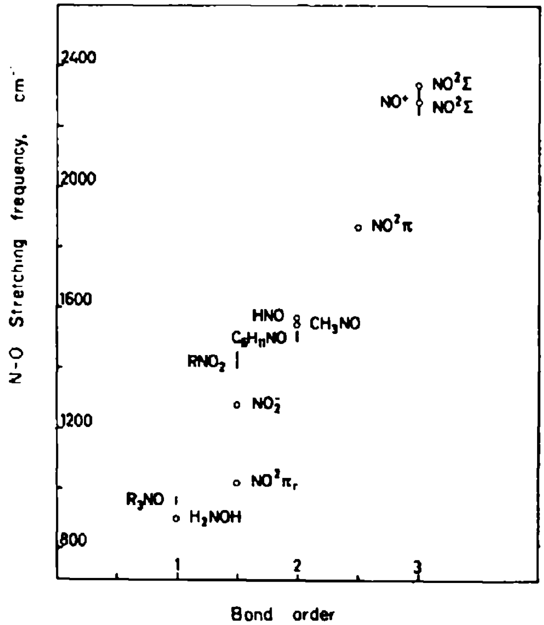

Fig. 1. Variation of NO stretching frequency with bond order.

In the trialkylamine oxides $R_3N—O$, the bond between nitrogen and oxygen must be a single electron-pair bond; the NO stretching frequency is in the range 950–970 cm^{-1}.[2] The NO frequency in hydroxylamine, $H_2N—OH$, is near 900 cm^{-1} and can also be assigned to a single bond.

The data for these reference molecules are shown in Fig. 1, in which the NO stretching frequency is plotted against the bond order. The bond order-frequency correlation exhibited here is in good agreement with similar data presented by Jonathan[20] and Millen and Polydoropoulos and Watson.[21]

NO *bond lengths and bond order*

The bond lengths may be treated in a similar way. The data used in constructing Fig. 2 are obtained from references 1 and 14. For bonds of order 3: 1·062 A in NO$^+$, and 1·064 and 1·075 in two^2 excited states of NO. For bonds of order 2½: 1·15 A in NO, 1·15 in BrNO and 1·14 in ClNO (the value 1·13 in FNO is less reliable).

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[17] D. M. Hirst and J. W. Linnett, to be published.

[18] I. C. Hisatsune, J. P. Devlin and S. Califano, *Spectrochim Acta* **16**, 450 (1960).

[19] J. W. Linnett, *J. Chem. Soc.* 275 (1956).

[20] N. B. H. Jonathan, *J. Mol. Spectroscopy* **4**, 75 (1960).

[21] D. J. Millen, C. N. Polydoropoulos and D. Watson, *J. Chem. Soc.* 687 (1960).

For bonds of order 2: 1·21 in HNO. For bonds of order 1½: 1·24 in NO_2^-, 1·22 in CH_3NO_2, 1·385 and 1·448 Å in the $^2\Pi_r$ excited state of NO.[14] For bonds of order 1: 1·36 or 1·44 in $(CH_3)_3NO$ and 1·46 in H_2NOH. The results are shown in Fig. 2. In the range from 4 to 6 bonding electrons the variation is regular. However for the bonds supposedly involving 3 electrons, the range of lengths is very wide and appears to overlap the range of lengths for bonds involving 2 electrons. As with the vibration frequencies, the experimental data are better at fixing the orders which are two (4 electrons) or greater, though lower frequencies and longer bonds are useful in deciding that the order is less than two. An explanation of the anomaly in NO_2^- might be that there is an effect of electrostatic forces in the crystal (it is the only ion that has been included). For nitromethane, the NO bond length may be shortened because of the formal charge of +1 on the nitrogen atom causing it to have a greater effective electronegativity compared with that in HNO, NO and ClNO.

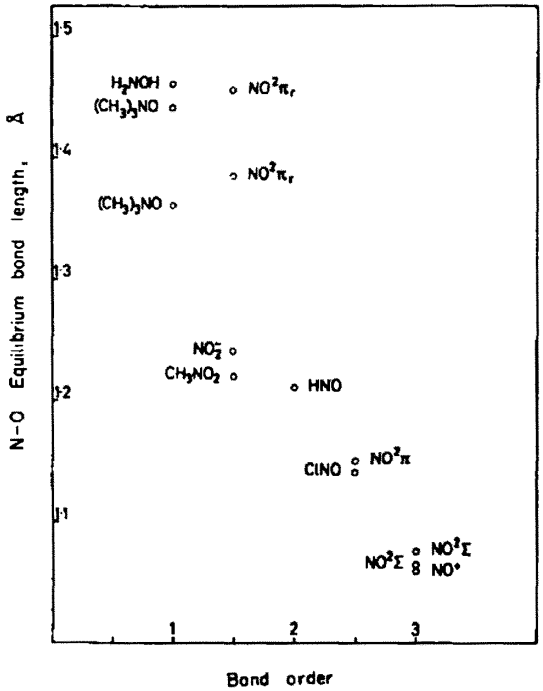
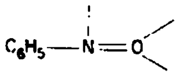


FIG. 2. Variation of NO equilibrium bond length with bond order.

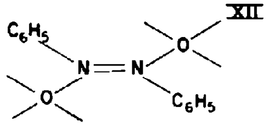
Dimerization of nitroso compounds

Nitrobenzene dimerizes very readily. The formula of the monomer will be expected to be XII. For the same dimer the possible formulae are XIII, XIV and its mirror image, XV and its mirror image and XVI. For all these the number of electrons in bond regions is the same, and twice that in XII, so that the reason for dimerization is not an increase in the number of bonding electrons.

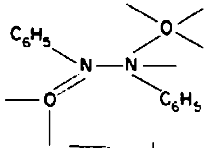
The various formulae for the dimmer will now be examined in detail, Formula XIII is unsatisfactory in that there are four pairs of electrons in the same bonding orbitals in the ONNO system and also the formal charge distribution is −1, +1,



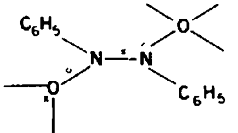
XII



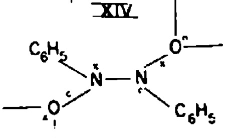
XIII



XIV



XV



XVI

$+1, -1$, On the other hand the electrons of each spin, tending to adopt a tetrahedral disposition round each atom, favour the same molecular shape. In XIV the formal charges are $0, +1, 0, -1$. On the other hand there are seven electron pairs in the ONNO system occupying the same bonding or lone pair orbitals so rendering inter-electron repulsion even greater than in XIII. The electron arrangement in XIV favours the atomic arrangement at one nitrogen atom being planar and at the other pyramidal. Because XIV and its mirror image would necessarily be involved, this is an unsatisfactory feature. In XV there is some separation of electron pairs (only one pair occupying the same bonding orbital), and the charge distribution is better than in XIII ($-\frac{1}{2}, +1, +\frac{1}{2}, -1$). On the other hand, at one nitrogen atom the electrons of one spin favour a different shape from that favoured by the other (planar and non-planar). At the other nitrogen, both favour the same shape. Formula XVI is the most satisfactory as regards charge distribution) $-\frac{1}{2}, +\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2}$) and there is only one pair occupying the same bonding orbital as in XV. However, at both nitrogen atoms, the electrons of one spin favour a different shape from those of the other (planar and non-planar). A priori, it is possible to conclude that XIII cannot be the structure of the dimer. Relative to two molecules of the monomer there is no advantage energetically and, in fact, there is the considerable disadvantage of the unfavourable charge distribution; XIV is also unsatisfactory. However, it is not easy to choose between XV and XVI, and perhaps one might be tempted to suggest that a hybrid of the three forms provides the best description (XVI and XV and its mirror image).

The NN bond length in $BrC_6H_4NONOC_6H_4Br$ is 1·31 (cf. in NH_2—NH_2, 1·47; in $NH_3^+NH_3^+$ (in which both nitrogen atoms have formal positive charges) 1·40; in $C_6H_5N{=}NC_6H_5$, 1·23 and $FN{=}NF$, 1·25 A), while the NO bond length is 1·35 A suggesting a bond order between 1 and $1\frac{1}{2}$. These data tend to imply that the structure is probably best represented by a hybrid of XV and its mirror image. However the characteristic NO frequency in the dimer is 1290 cm^{-1}.[2] This is characteristic of a bond of order $1\frac{1}{2}$. It shows clearly that XIII cannot be the structure, and, in fact, tends to favour XVI, though some admixture of XV and its mirror image might not affect the frequency very much. A redetermination of the bond lengths would be most useful; the existing data are not very accurate and the bond lengths could now be obtained with greater precision. At the moment, probably the best conclusion is that XVI and XV and its mirror image all contribute but the extent of the contribution of each is uncertain.

This suggests that nitroso-compounds having the structure I in the ground state dimerize because, by so doing, a spatial separation of electron pairs occurs so that inter-electron repulsion is reduced. On the other hand, the nitrosyl halides, which have the structure II, do not gain in this way because there is already a separation of pairs in the monomer and consequently dimerization does not provide any advantage. In NO itself there are no pairs occupying the same orbitals, but the dimer would involve coincident pairs; therefore dimerization does not occur.[11] The dimerization of NO_2 has also been considered elsewhere.[11] Hence it is possible to provide an explanation as to why some of these compounds dimerize while others do not. Moreover this explanation is consistent with the bond length and IR data.

On the basis of valence-bond structures which employ only Lewis-type formulae, it is difficult to provide a convincing explanation as to why C_6H_5NO etc. do dimerize. Presumably the explanation must be that in the monomer there is just a single structure, whereas the dimer is a hybrid of three (XIII, XIV and its mirror image). But this is not very convincing because, while the monomer formula gives zero formal charges on each atom, XIII and XIV involve high formal charges in the ONNO system. Moreover they all favour different shapes for the dimer. It is difficult then to see why dimerization takes place. On the other hand, the present hypothesis ascribes it to a reduction in inter-electron repulsion energy. Surprisingly enough, it supposes that C_6H_5NO is unstable because it *has* a Lewis structure in the CNO system (I) involving electron pairs; the nitrosyl halides are stable to dimerization because they do *not* have Lewis structures.

When HNO is produced from hydrogen atoms and NO, it is destroyed by

$$H + HNO = H_2 + NO.$$

However Harteck[22] found that the product of the reaction of hydrogen atoms with nitric oxide could be condensed in a cooled trap to give a solid which exploded, when it was warmed up, to give nitrous oxide and water. Taylor and Tanford[23] suggest the possibility of $2\ HNO = (HNO)_2$, followed by $(NHO)_2 = N_2O + H_2O$. By comparison with the behaviour of alkyl and aryal nitroso-compounds this seems very likely. The dimer would be expected to be a hydrid of structures analogous to XVI and to XV and its mirror image (with H replacing phenyl). In such a system it is easy to imagine that first one then the other hydrogen will migrate to one of the oxygen atoms to give H_2O, leaving N_2O. So the data on similar compounds and the above interpretation of the electronic structures makes the sequence of processes via the dimer a very possible one. It would be interesting to discover whether N_2O can be produced in the gas phase from NO and H.

Azoxy-compounds and nitrosamine

Compounds like azoxy-benzene contain an NO linkage which is usually written as a coordinate bond. In $CF_3{\cdot}NO{\cdot}N{\cdot}CF_3$ Jander and Haszeldine[24] gave assigned 1256 or 1282 cm^{-1} to the NO group. From Fig. 1, this implies that the bond contains three electrons and that the structure is XVII rather than XVIII. In XVII, the charge

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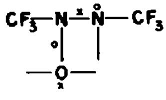
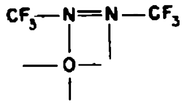
[22] P. Harteck, *Ber. Dtsch. Chem. Res.* **B66**, 423 (1933).
[23] H. S. Taylor and C. Tanford, *J. Chem. Phys.* **12**, 47 (1944).
[24] J. Jander and R. N. Haszeldine, *J. Chem. Soc.* 919 (1954).



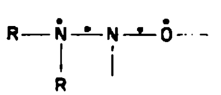
XVII



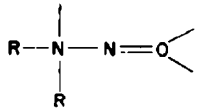
XVIII

distribution in the ONN system is $-\frac{1}{2}$, $+1$, $-\frac{1}{2}$, as against -1, $+1$, 0 in XVIII. This may be a more satisfactory distribution though a nitrogen atom would not be expected to assume a negative charge at all readily. However, the presence of the CF_3 group may render this less objectionable energetically. But, in addition, XVII reduces the number of electron pairs in the same bond or lone-pair orbitals compared with XVIII, so that XVII is favoured by a reduction in inter-electron repulsion. Probably these two effects are sufficient to make XVII preferred to XVIII.

In the dialkyl nitrosamines the atomic grouping NNO is also present. The NO characteristic frequency is 1430–1460 cm^{-1}. This implies that the structure is a hybrid of XIX and XX. The first has a formal charge distribution $+\frac{1}{2}$, 0, $-\frac{1}{2}$ in



XIX



XX

the NNO system, while that for XX is 0, 0, 0. On the other hand, all the electron pairs shown in XX occupy the same bonding or lone-pair orbital, whereas in XIX there is an almost complete separation of electron pairs into different orbitals. Thus the formal charge distribution favours XX while the consequences of interelectron repulsion favour XIX. It is not surprising therefore that the observed frequency indicates a bond order between 1½ and 2. The contrast with the azoxy compounds is interesting because, for them, the charge distribution and the separation of electrons favoured XVII. As a consequence it is understandable that the frequency in nitrosamines is higher than in $CF_3{\cdot}NO{\cdot}N{\cdot}CF_3$.

Excited states of nitroso compounds

Mason[25] has reported that in nitrosyl chloride the NO frequency of 1799 cm^{-1} in the ground state falls to 1580 cm^{-1} in the first excited state. This suggests that the structure II of the ground state passes to I in the excited state, the NO bond order becoming 2. Johnston and Bertin[26] have found a rather similar drop in frequency in FNO though, in this case, the decrease is rather greater (from 1844 to 1450). At the same time the NF frequency increases from 766 to 1086 cm^{-1}. This also implies that the structure changes from II in the ground state to something that is primarily I in the excited state. However, the small value of the NO frequency suggests that XXI may be of some importance. The conclusion that the NO bond becomes weaker and the NF bond stronger is supported by a study of the relative intensities of the different vibrational bands.

XXI

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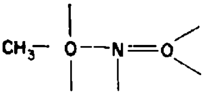
[25] J. Mason, *J. Chem. Soc.* 3904 (1957).

[26] H. S. Johnston and H. J. Bertin, *J. Mol. Spectroscopy* 3, (1959).

Mason has also shown that, in the halogen substituted organic nitroso compounds such as CF_3NO, C_3F_7NO, CCl_3NO etc. the NO frequency falls from about 1600 in the ground state to about 1350 or 1400 on excitation. This suggests that, on excitation, these compounds pass from an electronic structure I to one which resembles XXI. It is not known what happens to the CN frequency.

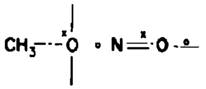
Alkyl nitrites

The simple formula of an alkyl nitrate is XXII. The two NO bond lengths in


$CH_3-O-N=O$

XXII

CH_3ONO are 1·37 and 1·22 A. There are consistent with XXII (Fig. 2). The frequencies of alkyl nitrites are however 1610–1640 and about 800. This suggests that there is some contribution to the structure from XXIII because the larger frequency is a little greater than expected for a double bond and the smaller one is a little smaller than that expected for a single one (Fig. 1). The formulae XXII and XXIII are

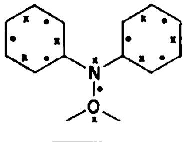

$CH_3-O\ N=O$

XXIII

analogous to I and II respectively. This means that the alkyl nitrites appear to have a structure which is primarily like that of an alkyl nitroso-compound but there is some contribution from the structure adopted by the nitrosyl halides. This is perhaps not surprising considering the ability of oxygen to assume a negative formal charge.

Diphenyl nitric oxide

This compound is paramagnetic, it is a relatively stable free radical. It has been suggested that the structure can be written as XXIV. The NO bond length in the *pp*′-dimethoxy derivative is 1·23 A which is consistent with the bond order being 1½ (Fig. 2) and therefore with XXIV. The characteristic frequency of 1350 cm^{-1}



XXIV

observed in the IR spectrum[27] also supports XXIV (Fig. 1).

Benzofuroxans and benzofurazans

The benzofuroxans were originally thought to be dinitrosocompounds (XXV). However experiments by various workers, NMR being employed most recently,[28] have shown that this is not the structure, but that the nuclear arangement is that in XXVI

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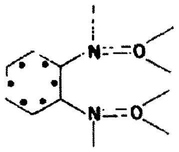
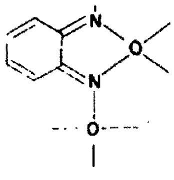
[27] W. Ottery and H. Kaimer, *Chem. Ber.* **87**, 1205 (1954).

[28] G. Englert, *Z. Naturforsch.* **166**, 413 (1961); A. R. Katritzky, S. Oesne, and R. K. Harris, *Chem. & Ind.* 1990 (1961).

(the electronic structure of XXVI is written in the manner of reference 28). However, it is difficult to see why the electronic structure XXVI should be preferred to XXV.

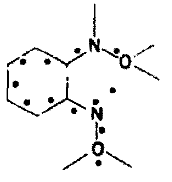


XXV

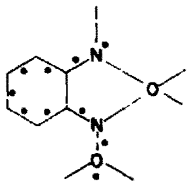


XXVI

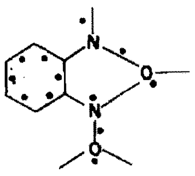
There is no change in the number of bonding electrons, and, in particular, there is the loss of a benzenoid ring and the assumption of formal charges on the atoms, whereas in XXV all the atoms have zero formal charges. One would therefore have expected XXV to be more stable than XXVI. However, there are other electronic structures one can write for the nuclear arrangement of XXVI. Some possibilities are XXVII, XXVIII and XXIX; there are other formulae of this type and also other Lewis type formulae in addition to XXVI.



XXVII



XXVIII



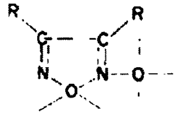
XXIX

Structures such as XXVII to XXIX would be expected to have a somewhat greater stability because, compared with XXV, there is, for all of them, a reduction in the number of pairs in the same bond or lone-pair orbitals, and hence a reduction in inter-electron repulsion. Unfortunately there are no bond-length data for this molecule and the spectra are very complicated and difficult to interpret. With benzofuroxan[29] there are several strong bands in the range 1400 to 1625 cm^{-1} and also some at lower frequencies which might be ascribed to the ONO part of the molecule. However, it is very possible that the magnitude of some of the characteristic frequencies may be seriously affected because the NO bonds are part of a ring. The frequencies of the analogous molecule XXX have been determined.[30] Frequencies that are associated with ONON part are 1475–1410 and

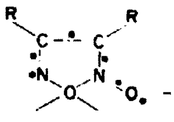
[29] J. H. Bayer, U. Toggweiler and G. A. Stoner, *J. Amer. Chem. Soc.* 79, 1748 (1957).

[30] N. E. Boyer, G. M. Germak, H. S. Gutowsky and H. R. Snyder, *J. Amer. Chem. Soc.* 77, 4238 (1955).

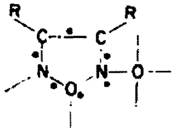
1360–1310. These are consistent with structures like XXXI and XXXII but not with XXXIII. On the hypothesis proposed the reason for the importance of XXXI and XXXII is that they result in a reduction in the inter electron repulsion energy.



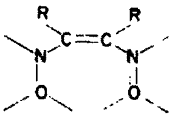
XXX



XXXI

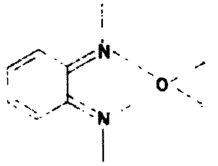


XXXII

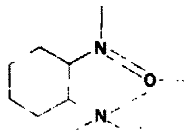


XXXIII

The structure of benzofurazan also presents some problems. The NO bond lengths are quite short (1·20 A)^1 which means that structure XXXIV is impossible even though it places a zero formal charge on each atom. Other possible structures

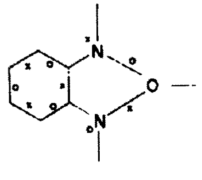


XXXIV

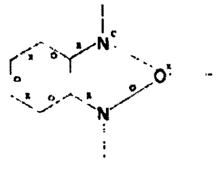


XXXV

are XXXV and its mirror image, XXXVI and XXXVII and its mirror image. Structure XXXV is most unlikely to be important because it puts a charge of -1 on the nitrogen atom. Structure XXXVI is most satisfactory in that it separates electron pairs and



XXXVI

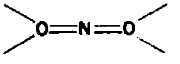


XXXVII

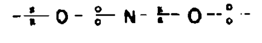
there is no difficulty regarding interbond angles. It has a slight disadvantage in putting charges of $-\frac{1}{2}$ on both nitrogen atoms and of $+1$ on the oxygen atom. Structure XXXVII is similar but perhaps more satisfactory in that the only formal charges are $-\frac{1}{2}$ on one nitrogen and $+\frac{1}{2}$ on the oxygen atom. It seems probable that XXXVI, XXXVII and its mirror image are the important structures though the NO bond length might have been expected to be a little greater (the accuracy of the measurements is not high). The CN bond lengths of 1·35 A (cf. $C_3N_3H_3$, 1·32 and $(CH_3)_2$ C=NOH, 1·29) are consistent with the above conclusions. The recorded CC ring bond lengths are all 1·43 A which seems surprisingly long. In the sulphur and selenium analogues the CN bonds are shorter and there are short CC bonds in the ring at positions corresponding to the double bonds in XXIV. This suggests that, in this compound, this is the structure, the reason being that sulphur and selenium are "unwilling" to assume a positive charge. As with benzofuroxan the complexity of the infra-red spectrum makes interpretation difficult.

The NO_2^+ *ion*

In this ion the NO bond length is 1·15 which is much less than for a double bond. The conventional structure is XXXVIII which would suggest a probable bond length of



XXXVIII



XXXIX

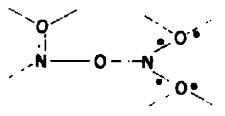
1·21 (as in HNO). Resonance with other Lewis structures may affect this conclusion. However, on the lines of this paper, a more likely formula is XXXIX, because it is anticipated that it would reduce inter-electron repulsion and it does not place any formal charge on the oxygen atoms. It is interesting that the CO bond length in CO_2 is 1·16 whereas that in formaldehyde is 1·23. The reduction is similar to that in NO_2^+. Because CO_2 will be expected to be analogous to XXXIX rather than to XXXVIII these data appear to be reasonable. The reductions in bond length when bonds such as those in XXXIX are involved in the structure is presumably a consequence of a reduction in inter electron repulsion so that the electron cloud can collapse a little with a consequent reduction in bond length.

The Raman effect shows that NO_2^+ has a symmetrical stretching vibration frequency of 1404 cm^{-1}. This is rather higher than the corresponding frequency of CO_2 showing that the force constant is greater. This is therefore consistent with the bond length. (The frequency must not be considered along with those in Fig. 1 because in this vibration the nitrogen atom is motionless).

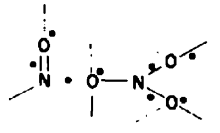
Oxides of nitrogen

Fateley *et al.*[31] have examined the IR absorption spectra of various oxides of nitrogen in solid matrices of carbon dioxide, argon etc. at low temperatures. They have interpreted their results in terms of the following characteristic frequencies: —NO_2 symmetric stretch: 1250–1300 cm^{-1}; NO_2 antisymmetric stretch: 1600–1760; —N=O: 1830–1900 cm^{-1}. One or two of their results will be considered on the basis of Fig. 1.

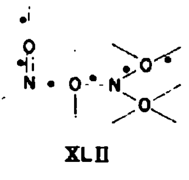
Condensation of NO_2 gives, along with other species, the dimer $ONONO_2$ to



XL



XLI



XLII

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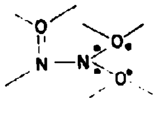
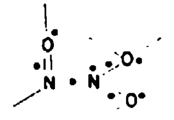
[31] W. G. Fateley, H. A. Bent and B. L. Crawford. *J. Chem. Phys.* 31, 204 (1959).

which Fateley *et al.* assigned the frequencies 787, 1290, 1645 and 1829. They assign the middle two to the NO_2 group and this is certainly justifiable. They assign 1829 to —N=O assuming the structure to be XL. On the basis of the hypothesis employed in this paper, there are other possible structures such as XLI and XLII which would be expected to be important because of the separation of electron pairs. Both these contain an NO bond like that in nitric oxide itself and it is the presence of this bond that we believe leads to the vibrational frequency 1829. Our proposed modification is therefore to the electronic structure, not to the nuclear arrangement.

Fateley *et al.* also concluded that they observed $ONNO_2$ having the frequencies 788, 1303, 1596 and 1867. The middle two were assigned to the NO_2 group, and 1867 cm^{-1} to —N=O in XLIII. An alternative structure in XLIV which contains an NO bond like that in nitric oxide so that a band at 1867 cm^{-1} is reasonable (cf. $ONONO_2$).

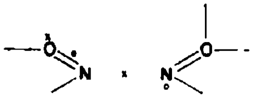


XLIII



XLIV

Smith *et al.*[32] found that liquid nitric oxide gave IR bands at 1770 and 1863 cm^{-1}. Fateley *et al.*[31] assigned frequencies of 1768 and 1862 cm^{-1} to *cis* ONNO. This *might* be expected to be a hybrid of the structure XLV and its mirror image. This might be expected to have symmetric and antisymmetric frequencies, the mean of which (1815) was a little smaller that that of the monomer (1876).



XLV

CONCLUSION

In this paper the structures of a wide varierty of compounds containing NO bonds have been discussed on the basis of the double quartet modification of the Lewis octet rule. The vibration frequencies and bond lengths have been used to assess bond orders. It has been found that a good broad description of the observations can be given if it is supposed that two effects which sometimes oppose one another, are important. These are: (i) that structures involving small formal charges on the atoms are preferred, and (ii) that those which dispose the two quartets differently in space round an atom are preferred to those involving "electron pairs" (i.e. two electrons in the same bond or the same lone-pair orbital).

Acknowledgements—One of us (J. W. L.) would like to thank G. Pimentel for a most helpful discussion of the structure of nitroso compounds and, in particular, of the nitrosyl halides, and also R. M. Acheson for his advice. The other (R. M. R.) is grateful to Lawrence College for a leave of absence and to the National Science Foundation for a Science Faculty Fellowship which made this work possible.

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[32] A. L. Smith, W. E. Keller and H. L. Johnston, *J. Chem. Phys.* **19**, 189 (1951).