Characteristics of Multiple N,O Bonds

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The electron distribution for N,O bonds in a wide range of molecules is analyzed using Bader's atoms in molecules theory and measures of bond order. It is shown that electron density derived parameters correlate very well with bond length and bond orders. An unexpectedly large number of bond orders are near to or greater than 2, indicating that nitrogen is effectively pentavalent in a many simple molecules. This conclusion is substantiated by examination of the Laplacian of the electron density. Such hypervalence indicates that nitrogen does not always obey the classical octet rule.

Introduction

Bonds between N and O atoms in molecules have a great range of lengths, showing an increase of about 40% from short ones such as in nitrosyl fluoride FNO (113.6 pm) to long ones as in fluorine nitrate $FONO_2$ (151.5 pm). They are also the subject of controversy concerning their simple theoretical description in terms of Lewis structures and the octet rule. As is well-known, their Lewis bond orders have a limited variety of values: conventionally 1, $1^1/_3$ (e.g., nitrate ion, NO_3^-), $1^1/_2$ (e.g., nitrite ion, NO_2^-), or 2 (e.g., nitrous acid, HONO), as a consequence of the strict application of the octet rule, which Pauling[1] emphasized as a necessity. However, their lengths are more varied than this simple picture implies, and are often inconsistent with their Lewis bond orders. Modern valence bond studies[2] have deduced that nitrogen utilizes five electron-pair bonds in at least some molecules, including FNO_2 and N_2O.

Earlier work with bonds of first row elements has shown varied correlations of electron density at the bond critical point, $\rho(r_c)$, with bond length. For CC bonds of about 30 hydrocarbons, Bader et al.[3] obtained a good linear correlation over the range from ethyne (C_2H_2) to ethane (C_2H_6), with points clustering about single, double, triple and benzene bonds. For the rather polar bonds of Be, B, and C with O in oxo and hydroxo compounds, Gillespie and co-workers[4] found good nonlinear (curved) correlations, but with no marked clustering around formally single or double bond lengths. They also showed that the geometry of the molecules of the period 2 atoms Be, B, C with O and F can be understood in terms of their Ligand Close Packing model, where the distances between nonbonded atoms are determined by typical ligand (atomic) sizes, resulting in a relatively fixed distance between the O and F atoms, and that these molecules are best considered as substantially ionic in character. The small size of the central atom means that the strengthening and shortening of one bond consequently leads to lengthening of the others. When N is the central atom the bonding is much less ionic,[5] but similar restrictions on the "inter-ligand" distance were found. They concluded that the C,O and N,O bonds in OCF_3^- and ONF_3 could best be described as double bonds, which contravenes the octet rule.

Molina and co-workers considered the bonding in ONF_3 as part of a study of bonding of the phosphoryl and related bonds in hypervalent molecules,[6] and concluded that the NO bond was a polar single bond. However, Chesnut[7] investigated the role of lone pairs in the bonding of these and other molecules, and concluded that the bond was best described as a polar triple bond.

In this study we shall utilize Bader's atoms in molecules theory[8] (as did the above studies) to investigate what influences the varying lengths of N,O bonds in molecules, and how this can be described by their bond orders, with consequent implications for their Lewis structures.

Electron Density, Bonds, Orders and Indices

Bader's atoms in molecules (AIM) theory[8] provides invaluable tools in analyzing the electron density in a molecule. The molecule is partitioned into atomic basins, whose boundary surfaces are ones of zero flux in the gradient vector field of the electron density. Two bonded atoms are linked by a bond path, which is the line of maximum electron density between their nuclei, and its minimum is at the bond critical point (BCP).[3] The electron density, ρ, always decreases away from a nuclear center, within its atomic basin, and without any local maxima.

A bond critical point lies on a boundary surfaces of the atomic basins, and the principle curvatures of the electron density (λ_1, λ_2, and λ_3) at that point have characteristic values. There is one positive curvature, λ_3, along the bond path, and two negative curvatures, λ_1 and λ_2, perpendicular to it, called a (3, −1) critical point in ρ. The sum of the three curvatures defines its Laplacian, $\nabla^2\rho(r_c)$, which is typically negative for covalent bonding. The ellipticity $\epsilon = \lambda_1/\lambda_2 - 1$ indicates any elliptical nature of the electron density, which for CC bonds can be related to π bonding.[9]

Using the more intuitive function $L(\rho) = -\nabla^2\rho(r)$, the maxima of $L(\rho)$ can be found and correspond to points where the value of ρ is more than that of its average in the neighborhood. These "shoulders" in ρ are called valence shell charge concentrations (VSCCs), and are (3, −3) critical points in $L(\rho)$.[10] The VSCCs show a notable correspondence to the hypothetical electron pairs in the VSEPR model of molecular geometry.[11] Also of interest are the (3, −1) critical points in $L(\rho)$, as these are "saddle points", corresponding to the minima between pairs of VSCCs, analogous to the bond critical points between atoms.[12]

The concept of bond order has a long history, intimately involved with a chemist's perception of molecules from the

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elementary concepts of bond orders in Lewis structures and in qualitative molecular orbital theory to sophisticated quantitative definitions. For ab initio wave functions it has been quantified in various ways, one of which, the Mulliken−Mayer (MMA) bond order, has its roots in Coulson's early proposals for π-orbitals at the Huckel level.[13] The Mulliken−Mayer bond order was shown[14] to derive from the exchange part of the second-order density matrix and has the expression:

$$B_{\mathrm{AB}}^{\mathrm{MMA}} = \sum_{\mu \in A} \sum_{\lambda \in B} (\mathrm{PS})_{\mu\lambda} (\mathrm{PS})_{\lambda\mu}$$

where **P** and **S** are the density and overlap matrices for the basis set, of which μ and λ are functions. The summations effect a partitioning in Hilbert space based on the atomic center for each basis function, following the concept of the Mulliken population analysis.[15] The bond orders obtained vary somewhat with the particular basis set, but for different molecules using the same basis set the correlations have been found to be reliable and useful (see, for example, Bridgemann et al.[16]).

Cioslowski and Mixon[17] subsequently proposed a bond order that was based on partitioning using the atomic basins defined by AIM topological theory. They defined their bond order as resulting from the diatomic contributions in a partitioning of the electron density after a localization procedure that maximizes the atomic populations while maintaining the first-order density matrix.

Ángyán, Loos and Mayer[18] showed that this bond order was almost identical to that derivable from the atomic partitioning of the exchange part of the second-order density matrix:

$$B_{\mathrm{AB}} = 2 \sum_{i,j} \{ n_i^{\alpha} n_j^{\alpha} + n_i^{\beta} n_j^{\beta} \} \langle \phi_i | \phi_j \rangle_A \langle \phi_j | \phi_i \rangle_{\mathrm{B}}$$

where *i*,*j* are the molecular orbitals, and $\langle \phi_i | \phi_j \rangle_{\mathrm{A}}$ is the molecular orbital overlap integral integrated over the atomic basin A and is an element of the topological atomic overlap matrix for atom A. They noted that this bond order was exactly twice Fulton's "sharing index",[19] defined to express the sharing of electrons between atomic basins.

Several authors pursued an alternative index,[20] variously based on the analysis of the pair population,[21] the fluctuation of the electron pair,[22,23] and the Fermi hole density,[24] with the latter group demonstrating that at the single determinant level they were equivalent to each other, and to the bond order[18] of Ángyán, Loos and Mayer. The bond order or index so defined measures the extent to which electrons associated with basin A are delocalized into basin B, and vice versa.[24] Consequently, the index only has a value of unity for an equally shared pair of electrons, and is sensitive to, and reduced by, the ionicity of the bonding between the atoms,[24] which for Cioslowski's localized molecular orbitals is readily expressed[25] as $(\langle \phi_i | \phi_i \rangle_{\mathrm{A}} - \langle \phi_i | \phi_i \rangle_{\mathrm{B}}) / (\langle \phi_i | \phi_i \rangle_{\mathrm{A}} + \langle \phi_i | \phi_i \rangle_{\mathrm{B}})$. Bader and co-workers pointed out[24] that a consequence was that the index could not be identified with a Lewis bond order, as the latter is the number of localized pairs of electrons between a pair of atoms, which, we might also note, is a pre-quantum mechanical concept. Accordingly, they called it the delocalization index. In the analysis presented here, the looser term bond order is used, as that is the term usually associated both with MMA and (Cioslowski) AIM bond orders.

Computational Details

All wave functions have been obtained using the Gaussian98[26] and GAMESS[27] suites of codes, the latter as implemented as PCGAMESS by Granovski,[28] using the B3LYP hybrid density functional[29] methods therein. Oberhammer[30] found that this method gave calculated N,O bond lengths in better agreement with experiment than did HF or MP2 methods, and this was confirmed. Dunning's cc-pVDZ basis set[31] was used, which is incorporated within Gaussian98, and was obtained from EMSL[32] for GAMESS. Coding within GAMESS provides the MMA bond orders, and within Gaussian98 provides the topological (AIM) bond orders using Cioslowski's localization method. Gaussian98 also provided the bond critical point information. MORPHY98[33] provided a full analysis of all critical points in ρ and $L(\rho)$, and the graphical representations of the Laplacians of the wave functions.

TABLE 1: Characteristics of N,O Bonds in Small Molecules[a]

	R_{exp}	R_{theo}	$\rho(r_{\mathrm{c}})$	MMA b.o.	AIM b.o.
NO_2^+	1.150	1.124	0.615	2.559	2.031
ONF_2^+	1.129	1.135	0.618	2.330	2.053
ONF	1.136	1.141	0.615	2.300	2.101
ONF_3	1.158	1.161	0.586	2.032	1.884
HON−O	1.177	1.173	0.568	2.173	1.930
FNO_2	1.180	1.183	0.548	2.115	1.761
$FON-O_2$	1.188	1.185	0.544	2.094	1.747
NNO	1.184	1.188	0.525	1.776	1.696
$HON-O_2$	1.210	1.198	0.531	2.029	1.705
NO_2	1.197	1.199	0.521	2.200	1.775
$HON-O_2$	1.210	1.213	0.513	1.953	1.629
NO_2^-	1.236	1.225	0.509	1.766	1.521
NO_3^-	1.222	1.261	0.459	1.764	1.475
CNO^-		1.264	0.436	1.551	1.327
$HONF_3$		1.317	0.412	1.329	1.181
ONH_3		1.337	0.367	1.388	1.186
$HO-NO_2$	1.406	1.411	0.322	1.235	0.963
HO−NO	1.433	1.429	0.300	1.331	1.026
$FO-NO_2$	1.515	1.523	0.245	1.121	0.728

[a] Experimental and theoretical bond lengths in Å; electron density at the bond critical point in au; bond orders

Results

The molecules considered cover the range of N,O bond lengths found in simple molecules, and the optimized geometries compare well with the experimental N,O bond lengths. Both 6-311G(2d,2p) and cc-pVDZ basis sets were used for geometry optimization, and as the latter gave slightly better results, only the results with cc-pVDZ basis sets are discussed further, but conclusions using the 6-311G basis set were similar. The experimental and calculated N,O bond lengths are given in Table 1, showing the generally close agreement achieved with the cc-pVDZ basis sets. Also presented in the Table are the MMA and AIM N,O bond orders. Table 2 gives the electron densities and their curvatures at the bond critical points for the molecules.

Figure 1a shows the excellent correlation between bond length and electron density at the bond critical point, $\rho(r_{\mathrm{c}})$. The electron density varies by a factor of 2 from single bonds such as formed by HO in HNO_3 and HNO_2, to those commonly considered to have double bonds (for example NO_2^+).

In Figure 1b we see the correlation between the electron density and its Laplacian, using $L(r) = -\nabla^2 \rho(r)$, which shows the general increase of the one with the other, a characteristic of covalent bonds with increasing conventional bond order.[9] Figure 1c shows how the curvature of ρ (using the eigenvalues λ_1 and λ_3) varies with the electron density. Again the set of N,O bonds shows the normal characteristics of covalent bonds, with λ_1 increasing compared to λ_3 as the electron density increases. It is also interesting to note that the ellipticity ϵ is

TABLE 2: Characteristics of the Laplacian at the Bond Critical Point[a]

	$\rho(r_c)$	$L(\rho)$	λ_1/λ_3	ϵ
NO_2^+	0.615	1.367	0.972	0.000
ONF_2^+	0.618	1.525	1.079	0.110
ONF	0.615	2.101	1.435	0.069
ONF_3	0.586	1.336	0.948	0.000
HON−O	0.568	1.650	1.177	0.080
FNO_2	0.548	1.172	0.941	0.087
$FON-O_2$	0.544	1.159	0.935	0.076
NNO	0.525	1.022	0.869	0.000
$HON-O_2$	0.531	1.111	0.927	0.104
NO_2	0.521	1.155	0.946	0.052
$HON-O_2$	0.513	1.030	0.903	0.106
NO_2^-	0.509	1.459	1.140	0.067
NO_3^-	0.459	0.853	0.861	0.118
CNO^-	0.436	0.786	0.829	0.000
$HONF_3$	0.412	0.797	0.860	0.107
ONH_3	0.367	0.395	0.670	0.000
$HO-NO_2$	0.322	0.364	0.703	0.158
HO−NO	0.300	0.218	0.618	0.083
$FO-NO_2$	0.245	0.014	0.552	0.195

[a] Electron density at the bond critical point and its Laplacian, both in au; ratio of curvatures; ellipticity.

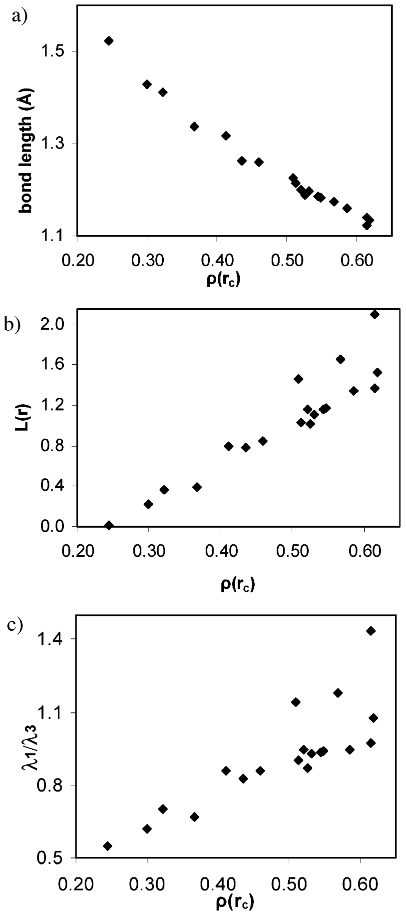

Figure 1. Variation of electron density at the bond critical point (atomic units) with (a) bond length (Å), (b) its Laplacian, (c) ratio of eigenvalues of the Laplacian.

consistently low, indicating that the electron density around a bond path is close to cylindrically symmetric for all the N,O bonds in the molecules.

Turning to bond orders (Figure 2), the MMA bond order correlates very well with electron density, whereas the AIM bond order shows a greater scatter, although the trend is very clear. As was noted earlier, although the MMA bond order does vary unpredictably with basis set, for comparisons within a "well-balanced" basis set it is found to perform well, as it does here.

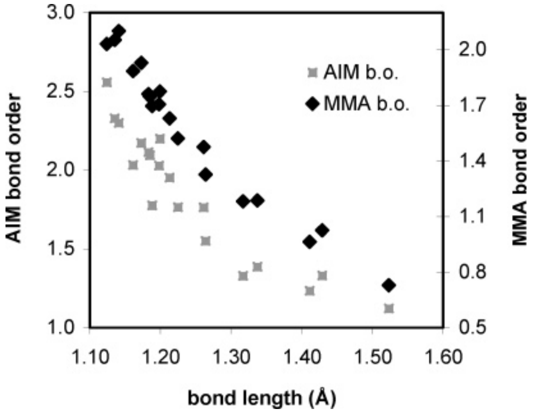

Figure 2. Variation of bond orders with bond length.

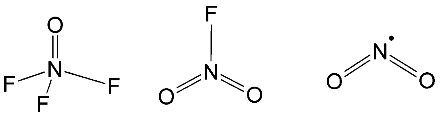

Figure 3. Lewis structures with double N,O bonds.

Discussion

1. Nature of N,O Multiple Bonds. The results here indicate that the physical properties (electron density at the bond critical point and bond length) of the N,O bonds in the set of molecules behave in a correlated and consistent way for bonds of a range of multiplicities. From Figure 1, it is evident that the electron density shows a steady and unbroken decline with bond length for N,O bonds conventionally described as multiple, from the highest value of about 0.62 (for NO_2^+ and ONF_2^+) to 0.51 (for NO_2^- and $HONO_2$). The only multiple N,O bond outside this set is the nitrate ion, and it is notable in that its calculated optimized bond length is substantially longer than the experimental value. When the electron density is calculated using the experimental bond length, its value increases to 0.506, bringing it to the end of the set. There is then a break before the single N,O bonds, with $HONF_3$ at 0.41, ONH_3 at 0.37, $HO-NO_2$ at 0.32, and HO−NO at 0.30. The N,O bond with the lowest electron density is that for $FO-NO_2$, at 0.245, which has the longest bond length (1.523). The varied lengths of the single N,O bonds can be understood in terms of Gillespie's ligand close packing model[4] as consequences of also having short multiple N,O bonds in those molecules.

Conventionally, the molecules ONF, NO_2^+, ONF_2^+ and HONO have Lewis structures with double N,O bonds, and have N,O bond lengths in the range 1.129 to 1.177, and electron densities from 0.618 to 0.568. The N,O bond in ONF_3 has length 1.158 and electron density 0.586, and so to be consistent should also have a Lewis structure with a double N,O bond, rather than the commonly ascribed single bond with charge separation, as has been pointed out by Gillespie.[5]

The molecules FNO_2, $FONO_2$, and NO_2, have slightly longer multiple bonds (1.180−1.197) and slightly lower electron densities (0.548−0.521) but still have AIM bond orders greater than 2, and MMA bond orders nearer 2 than 1.5, with those for $HONO_2$ only slightly outside these values. It would be quite consistent for these molecules also to have double N,O bonds in their Lewis structures, as shown in Figure 3 for FNO_2 and NO_2, along with ONF_3.

It is often expected that multiple bonds will show significant ellipticity, as is found for C,C double bonds.[9] However, the demands of molecular symmetry will prohibit this for bonds along a C_3 or higher symmetry axis, such as is the case for ONF_3. Further, Table 2 shows that the ellipticity of the *single* N,O bonds in $FONO_2$ and $HONO_2$ is larger than that found for *any* N,O multiple bond, including those conventionally described as double bonds (e.g., in HONO), so findings of low or high ellipticity are not a reliable guide to multiplicity of N,O bonds. It should also be noted, as Bader and co-workers have shown, that ellipticity varies along the bond path with heteropolar bonds, and can change sign,[34] so its value at the bond critical point can be misleading. Thus the ellipticity of N,O bonds does not give any guidance as to the multiplicity of the bonds.

From the basis of the observable properties of bond lengths and electron densities, as well as bond orders or indices, it is evident that many N,O bonds are better described as double rather than as than single, despite this contravening the octet rule. The implications of this for Lewis structures are considered further in the Conclusion.

2. Particular Case of ONF_3. In a study of Y_3XZ molecules ($Y = H$ or CH_3; $X = N$, P, As; $Z = O$, S), Molina and co-workers[6] also considered the possibility of π-bonding in ONF_3 from the geometry of its VSCCs. Three such are found in trigonal positions on the O atom, away from the N,O bond, and they concluded that this was evidence that π back-bonding did not take place. However, Chesnut[7] came to the opposite conclusion, by consideration of the contributions of (Cioslowski) localized MOs to the calculated AIM bond order. He found that such "lone pairs" in a variety of molecules are often significantly delocalized and contributing to the bond order. For ONF_3, he found that the two localized MOs that represent lone pairs on the O atom are significantly delocalized, with an ionicity of 66% each and contributed about half the total bond order.

Further investigation of the VSCCs associated with the O atom in the NO bonds produces an informative picture. The linear molecules all have a torus of maximum $L(r)$ for the O atom, a small distance on the further side from the N atom. For ONF_3 there are three VSCCs on the O atom, slightly away from the N atom (as found by Dobrado et al.[6]), but there is effectively a torus of maximum $L(r)$ with the three maxima ($L(r) = 5.693$ and $\rho = 0.938$) only slightly above the minima ($L(r) = 5.617$ and $\rho = 0.936$) − Figure 4. This is similar to the VSCC for the linear NO_2^+ ion, which is a torus of maximum $L(r)$, with the slight modification produced by the trigonal field of the three fluorine atoms.

For most of the other molecules where the O atom is probably multiply bonded to the N atom, there are two VSCCs located in the plane of the molecule, to the left and right of the O atom, and slightly away from the N atom (Figure 5). In contrast, the O atom VSCCs in presumably single NO bonds (in $FONO_2$ and $HONO_2$) are above and below the molecular plane.

It is of note that the distance of the plane of the VSCCs from their O nucleus (away from the N atom, the dfp as defined by Dobrado et al.[6]) correlates very well with the AIM bond order for the five molecules with C_3 or linear symmetry (NO_2^+, ONF_3, NNO, CNO^-, ONH_3) (Table 3 and Figure 6).

The correlation for planar molecules is also good, but over more restricted ranges (the distance ranges from 0.075 to 0.277 au for the first group, but only from 0.093 to 0.183 au for the planar molecules). As the magnitude of sharing or delocalization of electrons between the O basin and N basin increases, so does the distance of the VSCCs from the O nucleus. In this sequence, ONF_3 comes next to the NO_2^+ ion. It is likely that such increased sharing would result in a shift of electron density from the torus of charge concentration toward the N atomic basin. This would result in the center of charge concentration retreating in the opposite direction, as is found (the VSCC is not a maximum of charge concentration, but merely a "shoulder"). Further, although the radial distance of the VSCC from the O nucleus is almost

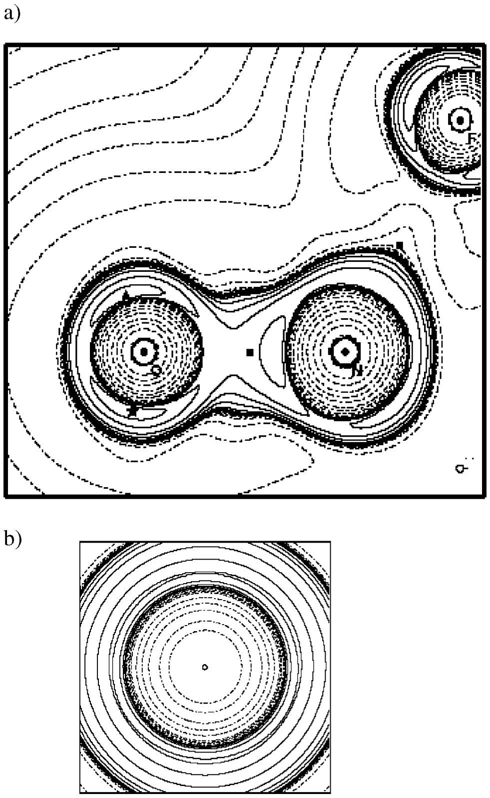

Figure 4. Laplacian of ONF_3 plotted in an ONF plane (a) and perpendicular to it through the CPs (b). ■, ∗, ▲ indicate bond critical points, and (3,−3) and (3, −1) critical points in $L(\rho)$.

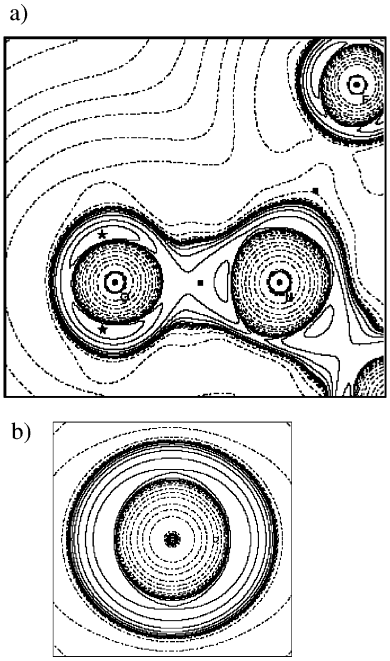

Figure 5. Laplacian of FNO_2 plotted in the molecular plane (a) and perpendicular to it through the CPs (b). ■ and ∗ indicate the bond critical points and (3,−3) critical points in $L(\rho)$.

TABLE 3: Characteristics of the VSCCs[a]

	CP type	ρ	$L(\rho)$	dfp	AIM b.o.
NO_2^+	(2, −2)	0.923	5.63	0.282	2.559
ONF_3	(3, −3)	0.938	5.69	0.181	2.032
	(3, −1)	0.936	5.62	0.189	
NNO	(2, −2)	0.948	5.99	0.142	1.776
CNO^-	(2, −2)	0.966	6.26	0.110	1.551
ONH_3	(3, −3)	0.998	6.93	0.074	1.388
	(3, −1)	0.997	6.90	0.074	
FNO_2	(3, −3)	1.032	7.52	0.117	2.115
	(3, −1)	0.857	4.29	0.273	

[a] CP, electron density at VSCC, its Laplacian, and distance of plane of VSCCs from O atom, all in au; bond order.

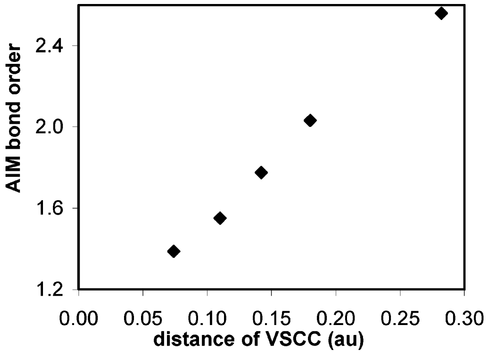

Figure 6. Variation of the distance of the plane of the VSCCs from the O nucleus with AIM bond order.

constant (0.626−0.620 au) the electron density at the VSCCs decreases, as is expected for a shift of electron density toward the N basin.

It should be remembered that a VSCC is not a Lewis lone pair, so its movement away from the N atom is not evidence that multiple bonding (π back-bonding in Pauling's terms) does not occur. Instead, the evidence of this fuller Laplacian analysis supports the contention that the N,O bond in ONF_3 is similar to that in NO_2^+ and should be considered multiple and not single. Chesnut's conclusion on the basis of the implications of ionicity of the three (Cioslowski) localized MOs was that the N,O bond was indicative of (polarized) triple bonding.[7] This is consistent with the results of the above analysis and with the (almost) cylindrical symmetry of the N,O bond of ONF_3. When it comes to a single Lewis structure to represent the bonding of ONF_3, perhaps it is best to follow Pauling's electroneutrality principle[1] and, like Gillespie,[5] focus on the double bonded structure of Figure 3, rather than a triple bonded structure with formal charges. This would be consistent with the accepted Lewis structures for NO_2^+ and CO_2, especially when noting that, like ONF_3, NO_2^+ has three (Cioslowki) localized MOs for each N,O bond, with rather less ionicity than ONF_3 (45% as compared with 66% for the two rather polar localized MOs).

Conclusions

We have shown for N,O bonds that ab initio bond orders have a very good correlation with bond length, and that the MMA bond order does better than the more securely theoretically based AIM bond order.

Further, the electron density at the bond critical point correlates very well with both the bond length and bond order. For apparently multiple N,O bonds, the electron density is close to cylindrical symmetry at the bond critical point, unlike that for C,C multiple bonds.

Again, unlike C,C bonds, the characteristics of N,O bonds change gradually from high electron densities and bond orders with short lengths to low electron densities and bond orders, showing no clustering at particular bond lengths. Those considered single bonds form a quite well-defined subset but still with a wide range of bond characteristics.

Writing acceptable Lewis structures for molecules such as ONF_3, and more generally for molecules commonly considered hypervalent, is contentious because, as Gillespie and co-workers have discussed,[5,35,36] the limitations of Lewis structures are often not recognized, and the meaning of the bond lines is ambiguous (do they imply polar or pure covalent bonds). The examples of triple bonds for ONF_3[7] and NO_2^+ above illustrate how conclusions from analysis of localized orbitals do not necessarily lead to reasonable looking Lewis structures. Appropriate Lewis structures for many of the molecules with nitrogen as a central atom involve hypervalent nitrogen, which contravenes the octet rule, supposed by Pauling to be inviolable for nitrogen atoms.[1] The rule, imposing a maximum of four pairs of electrons around an atom is often justified by reference to the four s and p orbitals of an isolated (hydrogen-like) atom. In simple classical valence bond approaches these are the only orbitals available for use, but the relevance of this to either simple pictorial illustration of the bonding in a molecule or to the conclusions of ab initio wave function analysis is less certain. Increasingly, the absolute nature of the rule has been questioned from consideration of the results of accurate wave functions, both molecular orbital[5,35,36] and valence bond.[37] Cooper and co-workers, using spin coupled valence bond (full-GVB) wave functions, showed that all five of nitrogen's electrons were involved in bonding in CH_2N_2, HCNO, N_2O[38] and FNO_2,[39] which, among other molecules, led them to their "democracy principle": "valence electrons can participate in bonding if given sufficient energetic incentives".[2] The results presented here give further support to the suggestion that the octet rule should only be regarded as indicative of the norm, rather than as an absolute prescription, even for first period elements. For nitrogen, the democracy principle of Cooper and co-workers is more appropriate, in that all five of the valence electrons are often involved in electron pair bonds, and the observable properties of the molecules are consistent with this. Another of Pauling's insights, the *electroneutrality principle*[1] provides an alternative to the octet rule, and is a very adequate guide for Lewis structures to represent bonding in molecules: quite simply, formal charges should be at a minimum. Even so, we should probably not expect complete consistency between analysis of ab initio wave functions of molecules and the pre-quantum mechanical concept of Lewis structures.

Note Added after ASAP Publication. This article was released ASAP on August 17, 2006. The first equation has been revised. The correct version was posted on August 22, 2006.

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