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THE RELATIONSHIP BETWEEN BOND TYPE, BOND ORDER AND BOND LENGTHS. A RE-EVALUATION OF THE AROMATICITY OF SOME HETEROCYCLIC MOLECULES

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Abstract - Traditionally, we have described the type of a bond in terms of its location along a continuum from single to triple bond. A review of the bond lengths of a variety of molecules (from the X-ray crystallographic data), along with VESCF calculations on some isoelectronic analogues of enamines, and their nmr spectroscopic data, indicated that bonds can only occur in integral units and that no bond can be of an intermediate type. This conclusion leads to a re-definition of aromaticity which definitively reveals the possible aromaticity of heterocyclic molecules.

Introduction

Unusual chemistry in carbohydrate[1a] and dihydrophthalide[1b] reactions have led us to explore the role of lone pair interactions in the chemistry of the oxygen heterocyclic compounds[1c-1h] and to examine the structural features of carbohydrate molecules.[1g,1h] In order to be able to examine rapidly the distances between centers not directly bonded together, the molecular graphics program STR3DI.EXE had also been developed[2a] and was used extensively[1g,1h] to facilitate the viewing of the X-ray crystallographic structures of organic molecules. This program can also automatically locate π atoms and aromatic systems using a bond length algorithm developed during that study.

All of the data from the crystallographic studies of carbohydrate and non-carbohydrate (natural and organic) molecules were totally consistent, and a number of important conclusions stated (and clearly implied) in the reviews[1g,1h] on the carbohydrate molecules are valid for all molecules and must again be stated briefly.

First, bond angle size in an organic molecule cannot consistently be related to the state of hybridization of the central atom, particularly when a heteroatom is attached to the central atom. Steric and electronic stress can often account for some of the unusual bond angles, but many cannot be easily explained.

Secondly, classical organic chemistry has suggested that bond types, and their closely related bond lengths (which should be within 1%-2% of the mean length), must fall into the following specific categories:

a) single bonds (longest bonds)
b) bonds intermediate in type and length between single and double
c) double bonds
d) bonds intermediate in type and length between double and triple
e) triple bonds (shortest bonds)

and that molecules which possess delocalizable π systems have bonds whose lengths should fall into the grey area between the single bond and double bond lengths (conjugated alkenes), or the double bond and the triple bond (conjugated alkynes).

However, the bond length data from many organic molecules revealed that the range of lengths of any given type of bond varied by more than 2% and was the length of that bond found in very simple molecules, or the sum of the covalent radii of the atoms, ± 7% of that value. This observation held very strongly for more than 99% of the single and double bonds in the (more than

350 natural and synthetic organic) molecules reviewed.

Further, the limits of the empirically determined 7% ranges of bond lengths for single bonds and double bonds, composed of a particular pair of atoms, were found to approach each other almost seamlessly but not to overlap. These ranges were not separated by an intermediate range/space. Only a few single bonds were found whose lengths did not fall within their specified ranges, and these were present in strained and unusual molecules.[1g,3] Therefore, these ± 7% bond length ranges were reliable criteria for assigning a bond type of single or double to any given bond.

While the data suggested that this 7% range might also apply to triple bonds, if the assumption that bond length ranges do not overlap is invoked, then the range of the length of triple bonds should be ± 6%, a logical inference based on the rigidity of triple bonds. However, it might well be that the double and triple bond ranges do overlap slightly and a future study of a larger number of molecules containing triple bonds will help to reveal this.

Thirdly, the fact that the bond length ranges for a given pair of atoms were not separated by intervals showed that the fractional bonds whose lengths were supposed to fall into intermediate length zones, between the normal bond ranges, cannot exist. This leads to the important conclusion that no bond can have type and length intermediate between that of a single and a double bond, or a double and a triple bond. Every bond does fall into a particular range of lengths corresponding to single, double, or triple, since there are no ranges of bond lengths that correspond to indefinite bond types.

Fourthly, by using an algorithm based on this ± 7% bond length range, STR3DI.EXE had reliably reconstructed and displayed the structure of several hundred molecule whose coordinate and atom type data (in any sequence of the atoms) had been input, and had automatically and correctly located the sites of π atoms and multiple bonds, and identified aromatic systems. It must be emphasized that the algorithms of STR3DI.EXE were based on empirical observations of molecular geometrical features, and three dimensional geometrical principles, and had nothing to do with quantum mechanics or molecular mechanics. The unqualified success of STR3DI.EXE confirmed the validity of the ± 7% bond range concept.

Bond Order and Bond Type.

One of the important, consistently reproducible, observations which emerged from the use of STR3DI.EXE was that any ring atom in a benzenoid aromatic system was attached to its two neighbouring ring atoms by bonds whose lengths were within the double bond length range. Thus, each of these ring bonds must have substantial double bond character,[1g,1h] consistent with the alkene-like chemistry of these molecules and the fact that each adjacent pair of atoms of aromatic systems can show alkene-like behavior.

This review therefore re-examines the relationship between bond order and bond type in π bonds involving the heteroatoms, using empirical data and VESCF π calculations,[4] which combination is much less likely to be subject to the possible flaws inherent in purely theoretical studies. By analyzing the bonding interactions in small organic molecules containing heteroatoms, one can develop an understanding of the factors which will enable these heteroatoms to participate in, or block, the formation of aromatic heterocyclic systems.

The Isoelectronic Analogues of the Allylic Anion.

Tables 1 and 2, below, show the results of the VESCF π calculations[4] on two groups of π systems analogous to (isoelectronic with) the allylic anion, based on the assumption that all of the atoms in these systems were π atoms (sp^2 hybridized). These simple molecules can be regarded as representative of important structural fragments which are often found in compounds which are possibly aromatic, and so the data they reveal will help us to fully appreciate the existence, or lack, of aromaticity in more complex heterocyclic (and homocyclic) systems.

Table 1 shows, in each group, the molecule which was predicted to display the most efficient $n-\pi^*$ delocalization at the top, and that with the least efficient n-π* delocalization at the bottom, of that group. Table 2 shows the calculated bond orders of the same two groups of molecules. MMX.EXE[4a] alternatingly minimizes the steric/electrostatic energy of the structure framework and does the VESCF calculations. Therefore, the final models presented by MMX.EXE were also the optimized geometries of the π systems.

Table 1.

MOLECULE[a,b]	ELECTRON DENSITY DISTRIBUTION AT π ATOMS					
(Numbering of π atoms) 1--2--3--4--5	1	2	3	4	5	6
CH$_2$=CH-CH-CH$_3$	1.4763	1.1632	1.3605			
O=CH-N(CH$_3$)$_2$	1.4496	0.8167	1.7338			
CH$_2$=CH-N(CH$_3$)$_2$	1.1286	1.0475	1.8239			
O=CH-O-CH$_3$	1.3376	0.7483	1.9141			
O=C(CH$_3$)-O-CH$_3$	1.4020	0.6813	1.9167			
CH$_2$=CH-O-CH$_3$	0.9591	1.0529	1.9879			
N#C-C(CN)=CH-N(CH$_3$)$_2$	1.14[c]	0.94[c]	1.2315	0.8784	1.7315	
O=CH-CH=CH-N(CH$_3$)$_2$	1.3390	0.7907	1.1645	0.9430	1.7627	
O=C(CH$_3$)-CH=CH-N(CH$_3$)$_2$	1.3921	0.7192	1.1757	0.9476	1.7654	
N#C-CH=CH-N(CH$_3$)$_2$	1.1419	0.9414	1.1753	0.9603	1.7810	
O=C(CH$_3$)-CH=CH-O-CH$_3$	1.3602	0.7030	1.0662	0.9337	1.9369	
benzene	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Table 2.

MOLECULE[a,b]	BOND ORDERS IN THE π SYSTEM					
(Numbering of π atoms) 1--2--3--4--5	1	2	3	4	5	6
CH$_2$=CH-CH-CH$_3$	1.6620	1.7315				
O=CH-N(CH$_3$)$_2$	1.8071	1.5613				
CH$_2$=CH-N(CH$_3$)$_2$	1.9111	1.4095				
O=CH-O-CH$_3$	1.9105	1.3280				
O=C(CH$_3$)-O-CH$_3$	1.8880	1.3315				
CH$_2$=CH-O-CH$_3$	1.9929	1.1068				
N#C-C(CN)=CH-N(CH$_3$)$_2$	2.94[c]	1.32[c]	1.7571	1.5468		
O=CH-CH=CH-N(CH$_3$)$_2$	1.8777	1.3921	1.8146	1.4985		
O=C(CH$_3$)-CH=CH-N(CH$_3$)$_2$	1.8659	1.3762	1.8219	1.4950		
N#C-CH=CH-N(CH$_3$)$_2$	2.9386	1.3200	1.8415	1.4755		
O=C(CH$_3$)-CH=CH-O-CH$_3$	1.8913	1.3140	1.9197	1.2589		
benzene	1.6667	1.6667	1.6667	1.6667	1.6667	

a) all disubstituted double bonds had the E configuration.
b) the symbol "#" represents a triple bond.
c) the electron densities on the atoms of the nitrile groups were very similar; this number is the average electron density.

The allylic anion was predicted to show the most delocalization and its C-C bonds should have bond orders of about 1.66. This clearly follows from the overall symmetry and atomic homogeneity of the framework. The bond orders and electron densities predicted for the allylic anion and benzene (also about 1.66) therefore provide us with a good frame of reference for appreciating truly delocalized systems.

The Role of Polarization of Heteroatomic π Systems.

The VESCF calculations, above, revealed that those molecules which possessed highly polarized π systems should display maximal delocalization processes, and their CH_3O-C and $(CH_3)_2N$-C bond orders should lie between 1.25 and 1.55. An examination of the interacting orbitals helps us to understand this feature, which will play a vital role in the discussions below.

In reality, a molecular orbital does not exist until the molecule is challenged, or perturbed, by the electron density which that orbital will be required to "accommodate". At that point, the system undergoes the structural changes necessary to allow the additional electron(s) to adopt the energy status which we have been able to understand by application of the principles of quantum mechanics. A discussion which refers to π*, or σ*, orbitals implicitly accepts this fact, but it is convenient to engage in these discussions as if these orbitals were already created, and sat waiting for the electron to arrive.

In the allylic anion, and its isoelectronic analogues studied, the atom bearing the lone pair of electrons is attached to the π bond and, since a p orbital has symmetry characteristics similar to both π and π* orbitals and the VESCF calculations assume that the lone pair of electrons are in a p orbital, we shall first examine this idealized π system.

The bond rotation process which brings the lone pair's p orbital into the same plane as the π* orbital, in order to effect orbital overlap and delocalization, also brings the lone pair's p orbital into the same plane with the electron rich π orbital. As the p orbital is rotated from a position orthogonal to the π bond, towards an eclipsed arrangement, the first effects are the repulsion of the p orbital electron density by the π bond electron density. In (or close to) the eclipsed arrangement the π* orbital will emerge since its spatial/electronic domain is challenged by the p orbital's electron density. If the p-π* interaction (controlled by the relative energies of these orbitals) is significant enough to cause a mixing of these orbitals then delocalization will occur, the overall energetic status of this eclipsed conformation will favourable/stable, and the eclipsed *conformation will persist, or have a long lifetime. If the p* and π* orbitals are not close enough in energy to allow mixing, then delocalization will not occur and the eclipsed conformation will still be dominated by the p-π repulsion, be unstable/repulsive, and be transient and of high energy.

If the π bond is polarized by some attached group, so that the end close to the p orbital bearing atom is electron deficient, then the situation is more favourable. Initially, the bonds attached to the electron deficient end of the π bond will be shortened by the increased electronegativity of that carbon. As the p orbital is rotated from an orthogonal, to the π bond, towards the eclipsed arrangement, the initial effect is an attractive dipolar interaction between the electron density of the p orbital and the electron poor terminus of the π bond. In the eclipsed arrangement the electrostatic interaction will be maximal at precisely the geometry required for maximal p-π* overlap and these energetically favourable effects will facilitate mixing of the orbitals, and delocalization.

Bonding in the MMX.EXE Optimized π Systems.

When STR3DI.EXE was used to display the optimized structures of the compounds listed in Table 1, it revealed that bonds whose orders were predicted to be in the range 1 to 1.5 had lengths within the single bond range of lengths, but bonds whose orders were predicted to be greater than 1.5 had lengths within the double bond range of lengths. Thus, in these systems, if p-π* interaction was efficient enough to achieve a bond order greater than 1.5 then a truly delocalized π system, with double bonds, existed, otherwise the system remained as a discrete π bond joined to the p orbital bearing atom by a single bond.

Undoubtedly, a double bond whose order is close to, but greater than, 1.5 will be very much weaker than a double bond whose order is much closer to 2, and so closer to optimal strength. However, if this bond order/bond type transition point is real, then even these very weak double bonds should show some double bond behavior, such as an observable restricted rotation about the weak double bond. This energy barrier to free rotation will be low, but must be higher than the normal barriers to rotation imposed by sterically controlled conformational preferences. Thus, this restricted rotation must be observable in the room temperature nmr spectra of these materials. Further, a bond whose order is greater than 1 but less than 1.5 should still display dominant single bond characteristics and not show restricted rotation.

Esters, Enol Ethers and the Anomeric Effects.

Esters ought to be the best possible situations for n-π* delocalization involving oxygen. However, the VESCF calculations show that only 8% of the available lone pair electron density would be delocalized. The vinylogous ester, 3-oxo-1-methoxybutene, was predicted to show a 6% delocalization of the available electron density of the oxygen's lone pair. For simple enol ethers, VESCF calculations reveal that the n-π* delocalization should be a marginal process since only 1% of the available electron density of the oxygen's lone pair should delocalized.

If the oxygen's lone pair is not in a pure p orbital (but in a sp^3 or similar hybrid orbital), then the delocalization will be much less efficient since the orbital symmetries would not be optimal for overlap. The lone pairs on oxygen have been represented as a σ-π pair.[5] However, there is evidence in support of the sp^3 hybridization of oxygen.[5] Thus, the extents of delocalization calculated by the VESCF method, which assumes p type orbitals, could be far more optimistic that will occur in reality. In any event, these calculations indicate the upper limit of the efficiency of the delocalization processes involving oxygen.

Most, if not all, n-π* delocalization processes must be much more efficient or favourable than n-σ* processes because of the energetic separations and the symmetries of the participating orbitals. If optimal oxygen n-π* delocalization is insignificant in the ground state of enol ethers and esters, then the much less favourable n-σ* processes cannot possibly be of any importance in the ground state of the simple acetals, and related molecules.

A comparison of the predicted efficiency of delocalization of the lone pair electron density on nitrogen and carbon with that on oxygen shows that the electronegativity of oxygen effectively limits the extent to which the lone pair is shared. Indeed, the VESCF calculations predict that the C1 of methyl vinyl ether is electron deficient, rather than electron rich, and this must be due to the strong perturbation of the molecular framework by the oxygen's electronegativity.

These VESCF calculations indicate that it is highly unlikely that any simple compound which has an oxygen atom attached to a π system will experience n-π* delocalizations with sufficient efficiency to give the C-O bond an order close to 1.5. Further, since there is no appreciable delocalization in the ground state of enol ethers, the nucleophilic reactivity of these molecules must be rationalized as a lowering of the activation energy for the formation of an intermediate oxonium ion by participation of the lone pair *after* the double bond has been attacked by an external reagent and the π bond is almost broken.

Finally, the nmr spectra of simple enol ethers[6] do not show restricted rotation about the carbon oxygen bonds, clearly indicating that these bonds have no double bond character.

Enamines and Amides.

The VESCF calculations suggest that dimethylvinylamine should display a C-N bond order of 1.4 and the electron density distributions shown in the Table 2. The nmr spectrum of dimethylvinylamine[6] shows one methyl resonance *indicating that this molecule* does show the free rotation about the C-N bond, typical of a single bond. Thus, as discussed above, the energies of the nitrogen's lone pair orbital and the adjacent π* *orbital energies are* not suited for overlap and the interaction between these orbitals must be transient, and overall repulsive. The characters of the interacting p and π, (π*) orbitals, and their parent atoms, will remain unchanged and the C-N bond is still a true single bond. Like enol ethers, the nucleophilic reactivity of these molecules must be rationalized as a lowering of the activation energy for the formation of an intermediate iminium ion by *participation of the lone pair after* the double bond has been attacked by an external reagent and the π bond is almost broken.

However, the n-π* interactions in the polarized molecules *dimethylformamide* and (dimethylaminomethylene)malononitrile (see Tables 1 and 2), attain enough energetic importance to enable these orbitals to mix and hence lead to the formation of true π systems (the C-N bond orders are greater than 1.5). Indeed, while the nmr spectra[6] of the enamine analogues (listed in the tables 1 and 2) whose C-N(CH_3)$_2$ bond orders were predicted to be less than 1.5 displayed rotation about the C-N bond, those enamine analogues whose *C-N(CH_3)$_2$ bond orders* were predicted to be greater than 1.5 displayed restricted rotation about the C-N bond and showed two methyl signals. Thus, the nmr spectra do confirm that a bond whose order is *greater than* 1.5 is a double bond (albeit quite weak if the bond order is close to 1.5), and that a bond whose order is less than 1.5 retains all of the physical features of a single bond.

Thus, VESCF calculations which predict a bond order greater than 1 but less than 1.5 indicate that even though the atoms could become involved in weak n-π* (or p-π*) interactions these interactions would be too weak to generate *formal π bonding and so* the atoms will retain their original characteristics. These bonds, whose orders are less than 1.5, are true single bonds.

New Criteria For Aromaticity.

Benzene is the archetypal aromatic molecule and the concept of aromaticity must be defined using this molecule. Each C-C bond of benzene has a predicted bond order of 1.67 and this clearly suggest that each atom in the aromatic ring is π bonded to its two neighbouring atoms. Further, the lengths of the C-C bonds in benzene do fall within the range of lengths of C=C double bonds. Atoms in aromatic systems are therefore formally pentacoordinated (while remaining tetravalent) and this feature of aromatic systems is that which truly distinguishes them from other, non-aromatic π systems.

Pentacoordination in tetravalent systems has long been invoked in the transition state of S_N2 reactions and 1,2-shifts (or non-classical carbonium ions) and is not a new concept. Indeed, if bond order is directly equated to number of bonds, and the orders of all of the bonds to any carbon atom of benzene are added together, then VESCF calculations suggests that each carbon atom of benzene enjoys a total of 4.333 bonds. Thus, regardless of one's theoretical preferences, the carbon atoms of benzene, and all other aromatic molecules, are not tetracoordinated. Since there is formal π bonding between every pair of neighbouring ring atoms in benzene, and therefore in every other truly aromatic molecule, an aromatic system must therefore be:

> Cyclic and each ring atom must be bonded to each of its neighbouring ring atoms by a bond whose length lies within the relevant double bond range. Thus, each ring atom would be formally pentacoordinated (lone pairs are regarded as substituents).

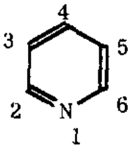
Alternatively, but congruently, an aromatic system must be:

> Cyclic and each ring atom must be bonded to each of its neighbouring ring atoms by bonds whose orders are greater than 1.5.

This model is quite consistent with that generated by molecular orbital theory, but differs from the description generated by the cannonical forms, hypothetical "molecules" with alternating double and single bonds, used in classical resonance theory.

Heterocyclic Aromatic Molecules.

Multiple bonding between two carbon atoms will be most efficient because of the identical sizes of the orbitals involved and the electronegativities of the atoms, and thus we appreciate the π bonding which leads to the aromaticity of some carbon compounds. The efficiency of π bonding between carbon and the heteroatoms is not as easily assessed and we are not always able to arrive at the correct status of π bonding, or the total number of delocalized π electrons, in a heterocyclic system. There has therefore been a great need for a simple method for assessing the presence, or absence, of π bonding in some very simple heterocyclic molecules whose aromaticity have been the sources of controversy, notwithstanding the multitude of modern tools which have been applied to these problems.[7] Since the new definition of aromaticity, stated above, does not require the explicitly knowledge of the number of delocalized π electrons in order to evaluate the aromaticity of any system, this definition resolves the uncertainties concerning the aromaticities of some heterocyclic molecules, shown below, whose known physical data and chemistry do not allow firm decisions to be made.



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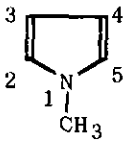

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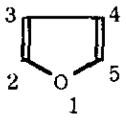

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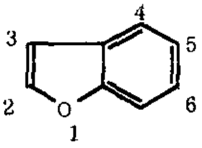

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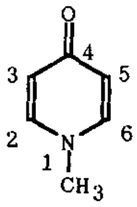

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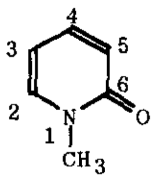

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Table 3 shows the lengths and orders for some bonds typically encountered in organic molecules.[1g,1h] As was stated earlier, the ± 7% ranges of lengths for bonds between any two types of atoms do not overlap and the Table 3 shows the upper and lower limits of the length of each bond type, at the boundaries, based on the 7% ranges. The limiting bond orders are those arrived at from the VESCF calculations, and discussions, above.

In the following analyses of the aromaticities of the molecules, shown above, MMX.EXE was used to calculate the minimum energy structure of each molecule and to provide the bond order data. STR3DI.EXE was then used to measure the bond lengths in the minimum energy structures. The bond lengths in the ground state, minimum energy structures are used, even though this experimentally determined data might be available,[7] because the application of this analysis to a hypothetical molecule must involve the use of the bond lengths of that minimum energy structure. There is little cause for concern about the accuracy of these bond lengths since it is well kown that MM2 and the derived programs are very successful in their ability to reproduce the structures of simple molecules with great accuracy.

Table 3.

Bond Type	Average Bond Length	Upper/Lower Bond Length Limit	Bond Order Range
C-C	154 pm	165 pm to 143 pm	< 1.5
C=C	134 pm	143 pm to 125 pm	1.5 to 2.5
C-O	140 pm	150 pm to 130 pm	< 1.5
C=O	122 pm	130 pm to 113 pm	1.5 to 2.5
C-N	148 pm	158 pm to 138 pm	< 1.5
C=N	129 pm	138 pm to 120 pm	1.5 to 2.5
C-S	188 pm	201 pm to 175 pm	< 1.5
C=S	164 pm	175 pm to 152 pm	1.5 to 2.5

Pyridine (1).

The C-N bonds in the minimum energy structure of pyridine should have lengths of 134 pm, well within the range of lengths for C=N double bonds, and orders of 1.65. The bond orders of the C2-C3 bond and the C3-C4 bond should be 1.67 and 1.66 respectively, very similar to those of the ring bonds of benzene. The bond lengths of the C2-C3 bond and the C3-C4 bond should be 140 pm, again very similar to those of the ring bonds of benzene and within the range of lengths for C=C double bonds. Thus, pyridine is a true heteroaromatic molecule, and its simple derivatives in which the π system has not been disrupted will be truly aromatic.

Pyrrole (2).

The C-N bonds of pyrrole should have bond lengths of 137 pm and bond orders of 1.503, which indicate that these bonds would just barely be within the range of lengths and bond order for C=N double bonds. The C2-C3 bond and the C3-C4 bond should have lengths of 139 pm and 141 pm respectively, within the C=C double bond range, and bond orders of 1.744 and 1.605 respectively. Pyrrole and its simple derivatives will therefore be aromatic molecule of modest aromaticity. Note that substituents which promote the delocalization of the lone pair from nitrogen will enhance the aromaticity of pyrrole, as discussed above.

Furan (3).

The C-O bonds of furan should have bond lengths and bond orders of 135 pm and 1.308, which indicate that these bonds would be well within the range of lengths and bond order for C-O single bonds. The C2-C3 bond should have length and bond order of 136 pm and 1.881, quite close to those parameters of a typical isolated double bond (134 pm and bond order 2.000). The C3-C4 bond should have length and bond order of 144 pm and 1.427, which demonstrate that this bond would be a single bond. Thus the molecule does not show the features of an aromatic system. Furan is not an aromatic molecule. Indeed, placing simple electron withdrawing groups at C3 and C4 does facilitate delocalization of the oxygen’s lone pair enough to cause the development of aromaticity in the ground state of furan. The chemistry of furan is known to be typical of a simple diene and/or enol ether.

Benzofuran (4).

The O1-C2 and O1-C7 bonds of benzofuran should have lengths of 135 pm, well within the range for C-O single bonds. These bonds should also have orders of 1.280 and 1.265 respectively. The C2-C3 bond should have length and order 136 pm and 1.906, respectively, values which are quite close to those of an isolated C=C double bond. Indeed, the calculated bond orders and bond lengths of the heterocyclic ring of benzofuran suggest that the bonds and electron densities in this ring should be more localized than the corresponding bonds and electron densities of furan. Benzofuran possesses an aromatic homocyclic ring, but the heterocyclic ring is not aromatic.

N-Methyl-4-pyridone (5).

The C-N bonds should have lengths and orders of 138 pm and 1.444 respectively. The C2-C3 bond similarly should have values of 137 pm and 1.835 respectively. Most interestingly the carbonyl group should have length and order of 123 pm and 1.821 respectively. These values clearly show that the 2-pyridone system is a localized system and is not aromatic. If delocalization leading to aromaticity were to be achieved, then the C-O bond would have been within the single bond range of lengths and have a bond order less than 1.5. Instead the values of length and order predicted are very similar to those of an isolated carbonyl group.

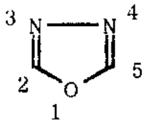
N-Methyl-2-pyridone (6).

The C-N bonds should have lengths and orders of 138 pm and 1.45 respectively. The C=O bond should have length and order of 124 pm and 1.780 respectively. These values clearly show that the 2-pyridone system is not aromatic.

Evaluations of Aromaticity of Novel Systems.

Clearly, from the above analyses, the concepts developed here are especially meaningful and significant in heterocyclic chemistry. Access to bond length data and/or to VESCF calculated bond orders for the energy minimized structures of any heterocyclic compound can now allow us to assess the aromaticity of that heterocyclic system and hence rationalize the stereo-electronic status, and hence the chemistry, of the system in its ground state.

For example, the molecules (7), (8), (9) and (10) are hypothetical entities whose syntheses might pose significant challenges and whose aromaticities might not therefore be easily assessed experimentally. The molecules (9) and (10) demonstrate the validity of the discussion above on the role of polarization of a π system in increasing delocalization in that system, here leading to aromaticity. Table 4 shows the bond orders, calculated by MMX.EXE, for the bonds in the molecules (7), (8), (9) and (10).



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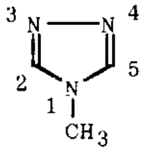

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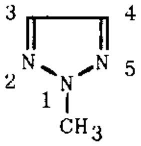

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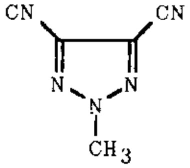

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Table 4.

Molecule	Bond Order Between Atoms						
	1		2		3		4
(7)		1.3124		1.9062		1.3348	
(8)		1.5037		1.7874		1.5098	
(9)		1.4963		1.7222		1.6356	
(10)		1.5158		1.7042		1.5746	

The molecule (7), like furan, would not be aromatic, again dramatizing the fact that simple, uncharged, oxygen heterocycles are unlikely to be aromatic in their ground state. On the other hand, the molecule (8), like pyrrole, would be aromatic.

The molecule (9) poses interesting questions because the orders of the ring bonds, except those to N1, are of the correct magnitudes for highly aromatic systems. However, the bonds to N1 are single bonds because of the localization of the lone pair on N1. It is quite likely that the molecule

(9), in an unperturbed state, would not show aromaticity. If the hydrogens on C3 and C4 are replaced by cyano-groups then the resulting molecule (10) is aromatic, as is shown by the orders of its bonds.

The transformation of a non-aromatic heterocyclic molecule into an aromatic molecule by attaching suitable substituents to the ring is probably a widespread phenomenon. Unfortunately, it is likely that a report on the aromaticity of molecule (10), which did not include an evaluation of the aromaticity of the analogue (9), would imply that the analogue (9) should also be aromatic, and this would be fallacious.

Transition States.

In the acyclic systems examined above, the VESCF calculations suggested that the lone pair bearing atom must participate in a 25% to 30% delocalization of one electron of the lone pair into the π system, in order to raise that bond's order to the critical limit of 1.5, and hence to transform the bond into a formal double bond. It is intuitively acceptable that the reverse must also be true, and that 70% to 75% of the electron density in a double bond must be removed, or that bond's order otherwise reduced to less than 1.5, in order to cause it to be converted into a single bond.

In general, the ± 7% bond length range logically leads to the conclusion that one must stretch any bond beyond its 7% limit, or otherwise reduce its bond order by 0.5 "bond order units" (for example from 1.0 to 0.5, or from 3.0 to 2.5), before that bond begins to be broken, or transformed into to its next, lower, type.

Since delocalization is not a dominant feature of the ground states of simple furans, benzofurans, enamines and enol ethers, it is clear that their nucleophilic reactions are processes in which the π bond must be perturbed, or attacked, by the approaching electrophile *before* the lone pair will participate, or become delocalized. The VESCF calculations performed on analogous compounds will provide valuable guidance as to the existence of true delocalization in their ground states and so allow a proper mechanistic appreciation of their chemistry.

Conclusions

No bond can be of intermediate character, for example, a half double bond (1 σ and 0.5 π), or a half triple bond (1 σ and 1.5 π). Bond order does not represent bond type, rather it guides us to recognize the point at which one type of bond is transformed into another. There is a fundamental relationship between bond order and bond length, namely:

a) all single bonds have bond orders less than 1.5

b) all double bonds have bond orders greater than 1.5 and less than 2.5

c) all triple bonds have bond orders greater than 2.5.

Bond types must therefore be strictly limited to integer values. In a formal sense, this concept recognizes the quantization of bond types, so endowing the progeny of electrons and nuclei with the fundamental quantum mechanical characteristics of their parents, at last.

These criteria are consistent with HMO theory and, in addition, they lead to a more rigorous definition of aromaticity. The aromaticity of new heterocyclic systems can now be predicted by calculating the orders of the bonds in their cyclic π atom arrays. The close relationship between bond order and bond length elaborated above also enables the aromaticity of new systems to be evaluated from its bond lengths, if the X-ray crystallographic structural data for that system is available.

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2a. STR3DI.EXE was written by the author (V.G.S. Box), for MSDOS compatible computers, in 1987. Copies of the most recently upgraded version, Ver. 3.10 (1991), can be obtained from the author.

2b. The X-ray coordinate data reviewed here, and previously,[1g,1h] was obtained from the Cambridge Crystallographic Database, many published papers and various texts on the crystallography of organic molecules.

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4a. MMX.EXE, version 88.500, produced by Serena Software (U.S.A.) from MM2 and MMP1, performs structure energy minimizations and VESCF π calculations. MMX.EXE was used on a MSDOS compatible computer. The program is available from Serena Software (contact Dr. Kevin Gilbert at 812-855-1302).

4b. For a discussion on the uses of programs like MMX.EXE see, T. Clark, "*A Handbook of Computational Chemistry*", John Wiley & Sons, New York, 1985.

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