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1,2,5-, 1,3,4- and 1,2,4-Oxadiazoles

A Theoretical Study of Electric Dipole Moments

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Discrepancies found for some oxygen-containing compounds in a recent VESCF study of dipole moments have been further investigated by studying in detail furan, oxazole, isoxazole, and three isomeric oxadiazoles. In a preliminary geometrical study it was found that the method described previously for estimating ring angles and bond lengths satisfactorily accounted for observed geometries. However in those compounds where more than one ring atom carries lone pair σ-electrons, the electrostatic forces originating in these lone-pair dipoles have a considerable influence on ring geometry. When this is incorporated in the geometrical treatment, good agreement with known geometries is obtained.

The effect of using Burns' rules for orbital exponents rather than Slater's rules to derive lone pair moments and the effect of including lone pair potentials in the hamiltonian have been studied. The best agreement between calculated and observed dipole moments (within 0.2 D) is obtained by using the BJ method that was used in the previous study but with revised values for some of the basic resonance integrals. The revised values are shown to be more in keeping with the relevant bond lengths and atomic numbers than the values previously used.

Die in einer VESCF- (PPP mit Elektronegativitäts-Variation) Untersuchung über Dipolmomente aufgetretenen Abweichungen bei einigen O-haltigen Ringen wurden untersucht. Bei Ringen, die mehrere einsame Elektronenpaare tragen, muß die kürzlich angegebene einfache Methode zur Bestimmung der Geometrie durch zusätzliche Berücksichtigung der elektrostatischen Kräfte zwischen diesen Elektronenpaaren erweitert werden. Die Burnsschen Orbitalexponenten führen bei den einsamen Elektronenpaaren zu besseren Ergebnissen, als die Slaterschen. Die besten Dipolmomente werden mit der sog. BJ-Methode erhalten (Fehler $<0{,}2$ D); allerdings wurden einige Resonanzintegrale gegenüber früheren Rechnungen abgeändert. Diese Resonanzintegrale entsprechen auch besser den Bindungslängen und Kernladungen.

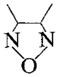
On a réétudié les contradictions trouvées pour certains composés oxygénés dans une étude récente des moments dipolaires par la méthode VESCF, en examinant en détail le furane, l'oxazole, l'isoxazole et trois oxadiazoles isomères. La méthode précédemment décrite pour l'estimation des angles du cycle et des longueurs de liaison rend compte de façon satisfaisante des géométries observées. Cependant dans les composés où plus d'un atome du cycle porte des paires libres d'électrons σ, les forces électrostatiques provenant de ces dipôles ont une influence considérable sur la géométrie du cycle. Lorsque l'on tient compte de cela dans le traitement de la géométrie, un bon accord est obtenu avec l'expérience.

On a étudié l'effet provoqué par l'usage des règles de Burns plutôt que celles de Slater pour les exposants orbitaux pour l'obtention des moments des paires libres ainsi que l'effet de l'inclusion des potentiels des paires libres dans l'hamiltonien. Le meilleur accord entre moments dipolaires calculés et observés (à 0,2 D. près) est obtenu en utilisant la méthode BJ utilisée dans l'étude précédente mais avec des valeurs révisées pour certaines intégrales de résonance fondamentales. Ces nouvelles valeurs sont plus consistances avec les longueurs de liaison et les nombres atomiques que celles précédemment utilisées.

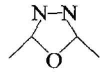
Introduction

In a recent study of conjugated systems by the VESCF-MO procedure, Brown and Coller [1] found that good agreement between observed and calculated electric dipole moments could be obtained for a wide range of molecules. It was noticed that the most significant discrepancies arose when oxygen was involved as a heteroatom in the five-membered ring systems such as furan, oxazole and isoxazole.

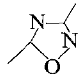
Recent spectroscopic studies of three of the four possible oxadiazoles [2, 3, 4] namely 1,2,5-oxadiazole (I), 1,3,4-oxadiazole (II) and 1,2,4-oxadiazole (III), by microwave methods have revealed values of dipole moments and structural information which may be used in a more comprehensive theoretical study of the role of oxygen as a member of a conjugated ring system.



1,2,5-oxadiazole (I)



1,3,4-oxadiazole (II)



1,2,4-oxadiazole (III)

The Extended Hückel Theory (EHT), as developed by Hoffman [5], when applied to these molecules leads to dipole moment estimates that are much larger than the observed values [6]. It would seem that though the EHT explicitly includes both σ- and π-electrons it should not be expected, in the present form, to predict dipole moments reliably because many of the approximations involved in the simple Hückel molecular orbital method for π-electrons are retained.

The VESCF method, though not involving self-consistent treatment of σ-electrons, appears generally to incorporate sufficient theoretical terms to yield satisfactory estimates of the distribution of net charge. The latter is formally associated with π-electron densities but appears in practice to represent the combined density of π- and σ-electrons.

We have therefore applied the VESCF method to the oxadiazoles to determine whether the discrepancies found for furan and the oxazoles again appear. Our earlier treatment of heterocyclic oxygen involved choice of the integrals by analogy with secondary nitrogen in a similar situation and it seemed likely that it could be necessary to reassess the values of theoretical quantities that refer to oxygen. One of the more sensitive tests of molecular wave functions is their ability to predict dipole moments and any improvement one obtains in this respect may be tentatively regarded as an improvement in the wave function itself. If it is possible to remove or even minimize the deviations for systems containing oxygen, while retaining the good agreement for the forty-odd other molecules already successfully treated, then the usefulness of the VESCF technique will be greatly extended.

Methods and Results

Choice of Bond Lengths

Since the molecular structures of furan, (I) and (II) have been accurately determined [7, 2, 3], the published data were used to obtain the atomic coordinates for use in the calculations.

For oxazole, isoxazole and (III), though inertial constants are available [8, 4], the complete structures have not yet been published. Bond lengths are readily estimated, by analogy with corresponding internuclear distances in the three compounds for which such data has been reported, with the exception of the 3–4 linkages in oxazole and 1,2,4-oxadiazole. These distances were taken to be 0.06 Å less than the corresponding distance in furan, other C–N bonds being shorter than C–C bonds by this amount. The choice of angles presents a more difficult problem which is discussed in the following section.

Estimation of Ring Angles in Oxazole, Isoxazole and 1,2,4-Oxadiazole

It was first established that the method of optimizing ring angles, the utility of which was previously shown for non-alternant hydrocarbons [1], could be successfully applied in the case of the five membered ring heterocycle, pyrrole. Interactions between net charges in the molecule were ignored. The molecule being planar, the reference (strainless) value for each internal angle at a ring atom was taken to be 120°. The bond angle distortion energy was taken to be proportional to the square of the deviation of the internal angle from the strainless value with the same force constant for each ring atom including nitrogen. Excellent correspondence between the optimum angles thus obtained and those experimentally determined was obtained [9].

Furan was treated similarly except that the reference angle for oxygen was taken as 111.07° equal to the bond angle in the unstrained dimethyl ether [10]. Again the optimized angles were in good agreement with the experimental data.

Analogous treatment of 1,2,5-oxadiazole and 1,3,4-oxadiazole, for which structures are known leads to estimates of internal ring angles that are closer to those observed in furan than to those observed in these systems. The reference angle for tertiary nitrogen was taken as 116.90° on the basis of data referring to N-methyl methylene imine [11]. These two heterocyclic systems contain three atoms carrying localized electric dipoles associated with non-bonded pairs of electrons. The electrostatic forces between these dipoles may constitute a significant contribution to the intramolecular strain. The total of bond angle distortion energies and electrostatic potential between atomic dipoles is then given classically in the point dipole approximation by

$$\begin{aligned} V_{\text{strain}}(\text{eV}) = {} & \sum_{\varrho} \tfrac{1}{2} K_{\varrho} (\theta_{\varrho} - \theta_{\varrho}^{0})^{2} \\ & + 0.6245 \sum_{\nu < \varrho} \mu_{\varrho} \mu_{\nu} r_{\varrho\nu}^{-3} \quad (2 \cos \phi_{\varrho\nu} \cos \phi_{\nu\varrho} - \sin \phi_{\varrho\nu} \sin \phi_{\nu\varrho}) \end{aligned} \qquad (1)$$

where

θ_{ϱ} is the internal angle at atom ϱ,
θ_{ϱ}^{0} the corresponding reference or strainless angle,
K_{ϱ} the force constant for distortion of the internal angle at atom ϱ,
μ_{ϱ}, μ_{ν} the atomic dipoles in Debye units at ϱ, ν,
$r_{\varrho\nu}$ the internuclear distance in Å,
$\phi_{\varrho\nu}$ the clockwise angle between the vector $r_{\varrho\nu}$ and the dipole vector on atom ϱ,
$\phi_{\nu\varrho}$ the corresponding angle at atom ν.

Minimization of this function with respect to all internal angles, for the known bond lengths in the two symmetrical oxadiazoles, with a single $K = K_{\varrho}$ for all ring angles as a parameter leads to $K = 2.9$ for 1,2,5-oxadiazole and $K = 4.0$ for

1,3,4-oxadiazole in units of (eV · radian^{-2}) which corresponds to the middle of the range of bending force constants, 0.2 to 0.5 mdyne Å/rad^2, normally found in normal coordinate analysis of vibrational spectra. The allowance for the variation of intramolecular electrostatic potential with change of ring angles thus reduces the apparent anomalies in the skeletal shapes of the symmetrical oxadiazoles. These findings provide evidence for an important influence of electrostatic interactions between atomic dipoles on ring shapes in heterocycles containing more than heteroatom with non-bonded electron pairs, which should also apply to unsymmetrical systems.

Table 1. *Molecular geometries*

Molecule	r_{12}	r_{23}	r_{34}	r_{45}	r_{51}	<512	<123	<234	<345	<154
Furan[a]	1.362 Å	1.361	1.431	1.361	1.362	106.55°	110.68	106.22	106.22	110.68
Isoxazole[d]	1.38	1.30	1.43	1.36	1.36	106.2	111.1	107.2	106.0	109.5
Oxazole[d]	1.36	1.30	1.37	1.36	1.36	102.4	115.0	104.8	107.9	109.9
1,2,5-oxadiazole[b]	1.380	1.300	1.421	1.300	1.380	110.40	105.82	108.98	108.98	105.82
1,3,4-oxadiazole[c]	1.348	1.297	1.400	1.297	1.348	102.07	113.40	105.57	105.57	113.40
1,2,4-oxadiazole[d]	1.38	1.30	1.37	1.30	1.36	103.4	107.6	112.0	103.0	114.0

[a] Ref. No. [7]. [b] Ref. No. [2]. [c] Ref. No. [3]. [d] Estimated as described in the text.

With bond lengths estimated as described above, the optimum bond angles for use in VESCF calculations on oxazole, isoxazole and 1,2,4-oxadiazole have been determined by minimization of strain energy taking a mean value of $K = 3.50$ (eV radian^{-2}). These distances and angles are listed in Table 1, together with structural data taken from the literature for the symmetrical systems. Support for these structures is available, since by assuming reasonable coordinates for the hydrogen atoms in these systems based on data available for furan, (I) and (II), close agreement with the inertial constants reported by Sheridan *et al.* [4, 8] is obtained.

Method BJ

The formulation of the VESCF atoms-in-molecules method has been documented in previous papers [12, 13, 14, 15, 16]. Only π-electrons are treated in detail but it has been shown that a compensation effect may operate so that the derived net charges are not sensitive to the dissymmetry of distribution of electrons involved in σ-bonding [1, 17]. The eccentric distribution of electrons that may be assigned to non-bonding atomic orbitals does however lead to a definite contribution to the resultant dipole moment. Of the variants of the method, we have used in the first instance "method BJ" wherein all neutral atom penetration integrals are ignored and the Mataga-Nishimoto formula [18, 19] is used to estimate two-centre repulsion integrals. This prescription has in the past given consistently better results for calculated dipole moments compared with other variants including "method CJ" involving the inclusion of neutral atom penetration integrals computed by means of Slater-type atomic orbitals.

The Pariser-Parr formula [20]

$$\beta_{CC} = -2517.5 \exp(-5.007 r_{CC})\ \mathrm{eV}$$

was used for carbon-carbon core resonance integrals. The other resonance integrals were taken initially as given by Brown and Coller [1], namely

$$\begin{aligned}\beta_{CO} &= -2.300\ \text{eV} = \beta_{CN} \text{ for pyrrole}\\ &= \beta_{NO} \text{ by analogy}\\ \beta_{CN} &= \beta_{CC} \text{ for the same internuclear distance}^1.\end{aligned}$$

The nitrogen-nitrogen core resonance integral, which is needed only for 1,3,4-oxadiazole, was set initially as $\beta_{NN} = 1.95$ eV $= \beta_{CC}$ for the same internuclear distance.

The core coulomb integrals $(\mu|T + V_\mu|\mu) = -I_\mu$ are obtained from the observed valence state ionization potentials of the constituent atoms by a procedure similar to the method outlined by Brown and Coller [1]. For tertiary nitrogen, =N–, and secondary oxygen, –O–,

$$I = (s^{1+x}p^{4-x}, V_3) \rightarrow (s^{1+x}p^{3-x}, V_2), \tag{2}$$

where $x = 1/(1 + \lambda^2)$, λ being the usual hybridization parameter evaluated from the geometry of the molecule by assuming that bonding hybrids are directed along internuclear lines and that the hybrid occupied by a non-bonding pair bisects the external angle (the latter choice defines the non-bonding hybrid of maximum *s* content). In this work with five-membered ring systems we have chosen $\lambda = 1.00$ throughout for *sp* lone pair hybrids. The actual angles in these systems give a calculated λ within 2 or 3% of this value. The valence state ionization potential is then allowed to vary as before as a function of the effective nuclear charge on each atom.

The effective nuclear charge, Z_μ, for each atomic orbital was derived either from Slater's rules or from those outlined by Burns [22]. The important difference between conventional SCF-MO and the VESCF-MO treatments is that the latter allows for the variation of the effective nuclear charge with the net charge of each atom.

In the calculation of the electric dipole moment, as in the self consistent evaluation of charge distribution, the σ-frame-work is assumed to be non-polar with the exception that moments due to electrons in lone pair orbitals are included in the vector sum along with the moments formally associated with the unequal distribution of π-electrons to obtain the resultant. This unbalanced atomic moment, arising from a second electron in a hybrid orbital, calculated by means of Slater functions is given by

$$\mu_{at} = 14.68\,\lambda/(1 + \lambda^2)\,Z_\mu \text{ Debye} \tag{3}$$

when the screening constants for 2*s* and 2*p* electrons are taken as equal.

The results listed in Table 2 using method BJ confirm the earlier conclusions that oxygen-containing heterocycles do not in general give good results for calculated dipole moments using the conventional VESCF procedure with the exception of 1,2,4-oxadiazole. In the table the net π-charges on each atom are in milliprotonic units and the numbering of the atoms proceeds counterclockwise

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[1] $\beta_{CN} = \beta_{CC}$ is based on the pyridine-benzene example where this equality appears to give reasonable eigenfunctions. It should be noticed however that r_{CN} (pyridine) = 1.340 Å and r_{CC} (benzene) = 1.397 Å, i.e. the difference in lengths for these two bonds is approximately 0.06 Å. This difference is consistently shown for CN vs. CC bond lengths of similar bond order. Comparing the oxadiazoles (I) and (II) gives a convenient example. It would appear that the covalent radius of nitrogen is about 0.06 Å less than that of carbon. Pauling reaches the same conclusions [21].

Table 2. *Calculated charge distributions and dipole moments for oxygen heterocycles. Method BJ* $\beta_{12} = -2.300$ eV

Molecule	Atomic charge, Q_μ, and dQ_μ/β_{12} (m. proton units)					Components and resultant dipole moments (Debye)						
	Q_1	Q_2	Q_3	Q_4	Q_5	$\mu_x(\pi)$[b]	$\mu_y(\pi)$	μ_x(at)	μ_y(at)	μ_{calc}	$d\mu/d\beta$	μ_{obs}
Furan[a]	178(−94)	− 35(+16)	− 54(+32)	− 54(+32)	− 35(+16)	0.00 D	1.37	−0.00	−1.61	0.24	+0.76	0.66 [23]
Oxazole[a]	184(−94)	20(+24)	−136(+30)	− 35(+26)	− 34(+16)	1.04	1.46	1.01	0.62	2.08	−0.58	1.50 [8]
1,3,4-oxadiazole	189(−98)	24(+24)	−119(+26)	−119(+26)	24(+24)	0.00	2.20	0.00	1.37	3.57	−0.70	3.04 [3]
1,2,5-oxadiazole	196(−98)	−105(+12)	7(+36)	7(+36)	−105(+12)	0.00	0.66	0.00	−2.78	2.12	+0.80	3.38 [2]
Isoxazole[a]	186(−96)	−122(+12)	4(+36)	51(+28)	− 16(+16)	−0.32	1.05	2.75	−0.71	2.45	+0.42	3.07 [8]
1,2,4-oxadiazole	192(−96)	−121(+12)	23(+32)	−134(+28)	40(+24)	−0.68	1.33	0.91	−0.06	1.29	−0.36	1.2 [4]

[a] These values differ slightly from those reported by Brown and Coller [1] because of small differences in the geometrical parameters employed.

[b] The dipole moment coordinates for furan, 1,2,5-oxadiazole and 1,3,4-oxadiazole are such that the *y*-axis bisects the bond angle with the oxygen atoms at the vertex. For oxazole, isoxazole and 1,2,4-oxadiazole the *x* coordinate is directed along the 5–1 bond.

Table 3. *Calculated charge distributions and dipole moments for oxygen heterocycles. Method BJM*, $\beta_{12} = \beta_{15} = -2.300$ eV

Molecule	Atomic charge, Q_μ, and dQ_μ/β_{12} (m. proton units)					Components and resultant dipole moment (Debye)						
	Q_1	Q_2	Q_3	Q_4	Q_5	$\mu_x(\pi)$	$\mu_y(\pi)$	μ_x(at)	μ_y(at)	μ_{calc}	$d\mu/d\beta$	μ_{obs}
Furan	214(−102)	− 76(+18)	−31(+34)	−31(+34)	−76(+18)	0.00	1.22	0.00	−1.61	0.39	+0.80	0.66
Oxazole	231(−102)	−123(+20)	− 4(+32)	−68(+34)	−37(+20)	−0.68	1.24	1.01	0.62	1.89	−0.50	1.50
1,3,4-oxadiazole	252(−106)	−102(+20)	−24(+32)	−24(+32)	−102(+20)	0.00	1.31	0.00	1.37	2.68	−0.82	3.04
1,2,5-oxadiazole	188 (−96)	− 31(+14)	−63(+34)	−63(+34)	−31(+14)	0.00	1.45	0.00	−2.78	1.33	+0.74	3.38
Isoxazole	203 (−98)	− 57(+16)	−64(+38)	−17(+30)	−65(+16)	−0.67	1.12	2.75	−0.71	2.12	+0.36	3.07
1,2,4-oxadiazole	219(−100)	− 11(+20)	−111(+38)	+17(+28)	−115(+18)	−1.00	1.04	0.91	−0.06	0.98	−0.60	1.2

from the oxygen atom. Close examination of the figures listed reveals three possible adjustments of the VESCF parameters that might be made to bring the calculated moments more into line with experiment. First, the inclusion of electrostatic potentials arising from the permanent atomic dipole moment may be warranted because of their importance in consideration of the molecular shape. Second, Table 2 indicates that an adjustment of the atomic moment due to the excess electron in the non-bonding hybrid of the oxygen atoms and possibly the nitrogen atoms may have the desired effect of increasing the total moment for furan, (I) and isoxazole and lowering the moment for (II) and oxazole. Third, the assumption that β_{CO} is equal to β_{CN} for pyrrole is possibly not satisfactory and new values for both β_{CO} and β_{NO} in these systems should be explored. Each of these possibilities is examined below.

Method BJM

When an atom carries a non-bonded pair of electrons the density function contains an unbalanced *sp* product that contributes to the computed neutral-atom penetration integral a term corresponding to the potential arising from the permanent dipole moment. Method CJ, involving the inclusion of neutral atom penetration integrals computed using Slater density functions, has in the past been found to be marginally less satisfactory than method BJ in which these terms were placed equal to zero. This is thought to be due to an overestimation of penetration terms when Slater type functions are used as the basis of the neutral atom. Nonetheless it would seem more consistent if method BJ were to include allowance for those parts of the penetration integrals that correspond to the classical potentials produced by atomic dipoles. That these terms may be significant is particularly evident in considering the internal angles listed for the oxazoles and oxadiazoles.

The method designated "BJM" thus includes in the diagonal elements of the Hartree-Fock hamiltonian of method BJ the potentials of atomic dipoles treated as classical point dipoles, while "non-classical" contributions to neutral atom penetration integrals are again consistently ignored.

Thus the diagonal elements of methods BJ and BJM have the functional relationship

$$F_{\varrho\varrho}(\text{BJM}) = F_{\varrho\varrho}(\text{BJ}) - 14.40 \sum_{\nu \neq \varrho} \mu_\nu \cos\phi_{\mu\nu} r_{\varrho\nu}^{-2} \tag{4}$$

where the symbols in the second term are defined as in Eq. (1).

The results of the calculations using method BJM are shown in Table 3. According to the dipole moment criterion, method BJM is seen to give a more reasonable representation of charge for furan, (II) and oxazole but the discrepancies for the other three heterocycles, wherein nitrogen atoms are adjacent to oxygen, are even greater than by method BJ[2].

Atomic (Lone Pair) Moments and Burns' Exponents

Table 2 indicates that the atomic moment due to an extra non-bonding electron in a hybrid orbital on the oxygen atom may be too small, since an increase in the oxygen lone pair contribution to the total moment would bring all the

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[2] The negative charge on atoms 2 and 5 in furan, calculated by this method, also exceeds that on atoms 3 and 4, indicating that this method may give a better indication of preferred sites of attack by electrophilic agents.

molecules listed in closer agreement with experiment. One possible method for accomplishing this would be to use Burns' prescription for the effective nuclear charge in Slater type basis orbitals [22]. Here different values of Z_μ are used for $2s$ and $2p$ electrons and evaluation of the dipole moment integral now leads to the expression

$$\mu_{\mathrm{at}} = 14.68\,\lambda(Z_{2s}Z_{2p}/Z_{\mathrm{av}}^2)^{5/2}/(1+\lambda^2)\,Z_{\mathrm{av}}\ \text{Debye} \tag{5}$$

where Z_{av} is the mean of Z_{2s} and Z_{2p}. Table 4 gives the atomic moments that one obtains for secondary oxygen and tertiary nitrogen by using Burns' exponents along with those calculated by (3) using Slater exponents. In Table 5 the effect of these new atomic moments using method BJ to calculate the π-moment is tabulated[3]. Again the improvements are scattered due to the fact that the nitrogen atomic moment is not always directed in the same sense as the oxygen atomic moment for these systems. There is also evidence from saturated compounds suggesting that the values for the atomic moments for oxygen and nitrogen are quite reasonable when Slater's rules are used for computing the effective nuclear charge[4].

Empirical Adjustment of β_{CO} and β_{NO}

By varying the value used for β_{CO} it was found that for method BJ a value of $\beta_{\mathrm{CO}} = -1.55$ eV led to calculated moments for furan, oxazole and 1,3,4-oxadiazole within 0.2 D of observed values. Values of β_{CN} were again taken as equal to β_{CC} for the corresponding bonds in furan. Trials with different values of β_{NO} showed that $\beta_{\mathrm{NO}} = -1.00$ eV, together with $\beta_{\mathrm{CO}} = -1.55$ eV, yields similar agreement between theory and experiment for all six molecules considered here, as shown in Table 6. On the other hand method BJM gave unsatisfactory values for the dipole of 1,2,5-oxadiazole for any negative value of β_{NO}: in addition the discrepancy between theory and experiment for furan, oxazole and 1,3,4-oxadiazole could not be reduced below 0.4 D.

It thus appears that method BJ again gives the most satisfactory account of the distribution of electric charge in this series of molecules but those resonance integrals that relate heterocyclic oxygen cannot be equated to the value of $\beta_{\mathrm{CN}} = -2.30$ eV for pyrrole [13] previously determined by the reference to the absorption spectrum.

Discussion of β_{CN}

As indicated earlier the replacement of CH by tertiary nitrogen in these conjugated systems leads uniformly to a reduction in the distance to adjacent carbon atoms of 0.06 Å, this change being equal to the difference in covalent radii as estimated by reference to non-conjugated systems. The procedure of equating β_{CN} to β_{CC} for analogous bonds thus corresponds to taking the constant in the exponent of the Pariser-Parr formula for β_{CC} to apply to β_{CN}, but with a different multiplier for the exponential.

It is interesting that Flurry *et al.* [33] have recently suggested a modification of the Pariser-Parr formula that amounts to almost the same dependence on type

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[3] To be consistent the π-calculation should also include Burns' formulated Z_μ in the ionization potential quadratic and monocentric repulsion integrals. The results in Table 5 however discourage this further treatment.

[4] See for example Table 1 in Brown and Coller's paper [1] illustrating this point for first row hydrides.

Table 4. *Atomic moments for oxygen and nitrogen in five-membered rings*

	$\lambda(108°)$	$Z_{eff}(Q=0)$ Slater	$Z_{eff}(Q=0)$ Burns		μ_{at}(D) Slater	μ_{at}(D) Burns
Oxygen	1.00	4.55	4.40 (2*s*)	3.95 (2*p*)	1.61	1.75
Nitrogen	1.00	3.90	3.75 (2*s*)	3.30 (2*p*)	1.88	2.08

Table 5. *Dipole moments of oxygen heterocycles calculated by method BJ using atomic moments as given by Burns' exponents*

Molecule	μ_{calc} (D)	μ_{obs} (D)
Furan	−0.38	0.66
Oxazole	2.17	1.50
1,3,4-oxadiazole	3.74	3.04
1,2,5-oxadiazole	−2.38	3.38
Isoxazole	2.81	3.07
1,2,4-oxadiazole	1.31	1.2

Table 6. *Calculated charge distributions and dipole moments for oxygen heterocycles. Method BJ*; $\beta_{CO} = -1.55$ eV, $\beta_{NO} = -1.00$ eV

	Atomic charges, Q (m. proton units) and $dQ/d\beta_{12}$					Components and resultant dipole moments (Debye)						
Molecule	Q_1	Q_2	Q_3	Q_4	Q_5	$\mu_x(\pi)$	$\mu_y(\pi)$	μ_x(at)	μ_y(at)	μ_{calc}	$d\mu/d\beta$	μ_{obs}
Furan[a]	+107 (−94)	−23 (+16)	−31 (+30)	−31 (+30)	−23 (+16)	0.00	0.81	0.00	−1.61	0.80	+0.72	0.66
Oxazole[a]	+112 (−100)	+39 (+28)	−113 (+32)	−16 (+24)	−22 (+16)	−0.74	1.00	1.01	0.62	1.64	−0.60	1.50
1,3,4-oxadiazole[a]	+116 (−96)	+42 (+24)	−100 (+24)	−100 (+24)	+42 (+24)	0.00	1.67	0.00	1.37	3.04	−0.72	3.04
1,2,5-oxadiazole[a]	+66 (−102)	−86 (+16)	+53 (+35)	+53 (+35)	−86 (+16)	0.00	−0.37	0.00	−2.78	3.15	+0.78	3.38
Isoxazole[b]	+88 (−51)	−113 (−2)	+49 (+31)	−31 (−2)	+7 (+20)	0.14	0.41	2.75	−0.71	2.91	+0.22	3.07
1,2,4-oxadiazole[b]	+94 (−45)	−113 (−4)	+63 (+29)	−114 (−2)	+70 (+20)	−0.16	0.77	0.91	−0.06	1.04	−0.02	1.2
1,3,4-oxadiazole[c]	+103 (−19)	+50 (+12)	−102 (−3)	−102 (−3)	+50 (+12)	0.00	1.64	0.00	1.37	3.01	0.04	3.04

[a] Simultaneous variation of β_{12} and β_{15} in $(d/d\beta)$.

[b] Variation of β_{12} only in $(d/d\beta)$.

[c] $\beta_{34} = -1.25$ eV with variation of β_{34} in $(d/d\beta)$.

of nucleus and internuclear distance as the one described above. However the same formula cannot apply when nitrogen has a core charge of +2 since it would imply that β_{CN} in pyrrole should be −1.80 eV rather than −2.30 eV.

Consideration of β_{CO}

Comparison of the structures of dimethyl ether [11] and trimethylamine [24] indicates that the covalent radius of oxygen is a further 0.06 Å less than that of nitrogen, yet the difference between CO and CN distances in furan and pyrrole is only 0.02 Å. It is thus reasonable that β_{CO} in furan and the oxazoles should be less negative than β_{CN} in pyrrole, though the relative values empirically determined above are only qualitatively related by the exponential factor in the Pariser-Parr formula. It may be regarded as fortuitous that the formula leads to $\beta_{CO} = -1.50$ eV, which is close to the empirical value, when β_{CO} is equated to β_{CC} at a CC distance 0.12 Å greater than r(C–O) since no simple explanation is available for the apparent extension of the CO bond in furan and considering that the oxygen differs from carbon in core charge.

On the other hand the NO distance in 1,2,5-oxadiazole and the NN distance in 1,3,4-oxadiazole are 0.08 to 0.09 Å longer than would be expected on the assumption that the covalent radius of nitrogen is 0.06 Å less than that of carbon. It is possible to understand the extension of these internuclear distances on the basis of repulsion forces between adjacent atomic dipoles operating against a bond stretching force of about 9 mdyne $Å^{-1}$.

Insertion of the estimated increments into the Pariser-Parr exponential as a guide to the values of β_{NO}/β_{CO} and β_{NN}/β_{CC} leads to estimates of $\beta_{NO} = -0.98$ eV and $\beta_{NN} = -1.23$ eV. This value of β_{NO} is exceedingly close to the empirically found optimum value, while the last line of Table 6 shows that if β_{NN} is taken to be −1.25 eV there is little alteration in the overall calculated dipole moment although there is some redistribution of charge. Since nitrogen and carbon in these situations do not differ in core charge the exponential formula may be applicable.

It thus appears that the empirical core resonance integrals for use in method BJ that lead to such excellent agreement between observed and calculated dipole moments may be understood after detailed consideration of bond lengths is made. When atoms of unit core charge are being compared the results indicate that relative values of resonance integrals may be estimated by use of the exponential distance dependence in the Pariser-Parr formula.

General

It has been previously suggested, on the basis of Hückel MO and VESCF studies, that the relatively low reactivity of dibenzofuran toward electrophils compared to carbazole [27, 28] is primarily a function of the greater electronegativity of oxygen. It would now appear that electron delocalization from oxygen is also reduced by a lower resonance interaction. The much smaller degree of electron release from the hetero-atom and consequent lesser aromatic character, also ties in with the tendency of furan to behave as a diene showing 1–4 addition reactions with bromine and with maleic anhydride [25, 26].

Conclusions

It now appears that in previous VESCF-MO calculations the procedure of setting $\beta_{CO} = \beta_{CN}$ (pyrrole) in oxygen containing heterocycles is not justified, based on the discrepancies observed when a ground state property such as the dipole moment is calculated. Other assumptions, such as the inclusion of dipole potential contributions to the penetration terms in the Hamiltonian and the use of Burns' rules for computing the effective nuclear charge in determining atomic moments are seen not to improve the calculated results in any uniform manner. This is gratifying since both of these variations of the procedure would necessitate reassessment of the calculations for many of the molecules previously treated [1].

Thus the single value for $\beta_{CO} = -1.55$ eV used with method BJ of the VESCF procedure is appropriate to reproduce the electric dipole moments of five compounds containing oxygen in the ring system while $\beta_{NO} = -1.00$ eV yields good results for the three compounds to which it is applicable. The lesser magnitudes of these integrals may be understood from consideration of the relevant bond lengths, presumed to be lengthened by electrostatic interaction of atomic dipoles.

It seems paradoxical that the geometrical structures of the oxazoles and oxadiazoles may be understood when the interaction of atomic dipoles are considered, yet the electric field of these regions of local polarity do not appear to influence the distribution of π-electrons. Probably the σ and inner shell electrons on other atoms are polarized by these fields in a sense opposite to the drift of π-electrons and that the two charge movements largely compensate each other. The EHT treatment of these systems by Adam and Grimison [6] confirms these opposing polarities of σ- and π-electrons even though quantitative predictions of dipole moments using EHT in its present state seem remote. Other more reasonable all-valence electron treatments such as the CNDO method of Pople, Segal and Santry [29, 30] in preliminary calculations appear quite promising for predicting dipole moments [31], and again the indication seems to be that in systems with local electric potential created by essentially lone pair electrons, the polarization of σ- and π-electrons are in the opposite sense tending to cancel one another. It becomes increasingly clear that the VESCF π-only method gives estimates of atomic net charges rather than π-electron densities as previously thought. If this is the case then the present reassessment of the core resonance integrals β_{CO} and β_{NO} for heterocyclic systems appears to be a considerable advance in the VESCF and other SCF π-only treatments.

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