On the Determination of Bond Angles of Triatomic Radicals from Electron Spin Resonance Data

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Ab-initio UHF and complete CI calculations using minimal basis sets of atomic orbitals have been made for the neutral radical BH_2 and the isoelectronic series of radicals N_3^{2-}, NO_2, CO_2^-, BO_2^{2-}, and BF_2. The purpose is to test theoretically the reliability of an equation derived by Coulson linking the bond angle with the orbital hybridisation on the central atom. It is concluded that this equation is qualitatively reliable.

FROM the orthogonality conditions derived by Coulson,[1] the bond angle ϕ of a triatomic σ radicalo f C_{2v} symmetry is given by (1) where $\tau = C_p/C_s$ and C_s and C_p are the

$$\phi = 2\cos^{-1}(\tau^2 + 2)^{-\frac{1}{2}} \qquad (1)$$

respective coefficients of the valence *s* and *p* orbitals on the central atom X in the orbital of the unpaired electron. This equation has been widely used [2] to estimate approximate bond angles from e.s.r. data when both the isotropic (A) and anisotropic ($2B$) hyperfine coupling constants for the central atom are known.

The normal procedure, to obtain C_s and C_p, is to divide the experimental A and $2B$ values for the central atom X of the radical XY_2 by the corresponding A^0 and $2B^0$ values for the atom X in states where the outer *s* and *p* orbitals have unit population. These atomic values are either known experimentally or have been calculated from wavefunctions for the central atom.[2] Although this step is qualitatively reasonable, errors may be introduced if, on molecule formation, the character of the atomic orbitals, in particular, when close to the nucleus, is modified. This may be more significant for charged radicals. The C_s and C_p values are then fed into equation (1) to give an estimate of the bond angle.

Strictly this simple procedure must be approximate if only because the overlap of atomic orbitals between X and Y has been ignored in the derivation of the orthogonality conditions. However, inclusion of overlap does not seem to seriously alter the qualitative features predicted by equation (1). The generality of equation (1) has proven to be very useful to experimentalists who are often concerned with the task of identification,[2] the accuracy of the predicted angle ϕ being only of minor importance. The least to be expected of equation (1) is that trends in changes in bond angles will be faithfully reproduced, and in this respect the equation has been linked with Pauling's electronegativity rule [3] to study predicted bond-angle changes as a function of the electronegativity difference, $(X_X - X_Y)$, in XY_2 and XY_3 σ radicals.[2,4,5]

The problem is to obtain an unequivocal test of equation (1) over a whole series of radicals with widely differing electronegativity differences and angles ϕ. Since experimental verification has not been forthcoming, due to an inability to measure the geometry of most radicals using standard techniques, attempts have been made recently to provide a theoretical test of the validity of equation (1).[6,7] The results of INDO SCF-MO calculations for the radicals CO_2^- and BF_2 led to the conclusion that equation (1) is quite unreliable, even in a qualitative sense.[6] This study was strongly supported by Takahata *et al.*[7] by applying the 'point-charge model' [8] to the problem.

Because of the uncertainties already described in the evaluation of τ^2, the primary objective is to examine the interpretation of the theoretical evidence which led to the conclusion that equation (1) is qualitatively unreliable. In this sense we are trying to restore the position of equation (1) to its status before the appearance of ref. 6, *i.e.* of qualitative importance for the experimentalist.

CALCULATION

Although the ability of the INDO SCF-MO method to reproduce the e.s.r. parameters for these radicals is not being questioned, it was decided that the *ab-initio* unrestricted Hartree–Fock (UHF) method was more appropriate for a theoretical test of equation (1). The UHF method has been shown [9] to be reliable for reproducing e.s.r. parameters for second-row elements when using a minimal basis set of SCF atomic orbitals. This is convenient because direct comparison with the approximate INDO molecular-orbital method can be made. Each basis orbital is expressed as a linear combination of gaussians after Huzinaga,[10] 9*s*, 5*p* type for the heavy atoms and 6*s* type for hydrogen. Some calculations were made using the configuration interaction (CI) method to assess the effect of spin contamination in the UHF wavefunctions, after the quartet spin state is annihilated. For the 17-electron XY_2 σ radicals all the singly excited and doubly excited configurations necessary to ensure a doublet spin-state wavefunction were included. For the smaller BH_2 radical complete CI wavefunctions were studied, *i.e.* including all the possible excited configurations.

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Bond lengths were optimised for the radicals CO_2^- (Figure 2) and BH_2 (Figure 3). Suitable values were selected for the remaining radicals and are listed in Figure 1. Optimisation of the orbitals was only attempted for the hydrogen orbitals in BH_2 (Figure 3).

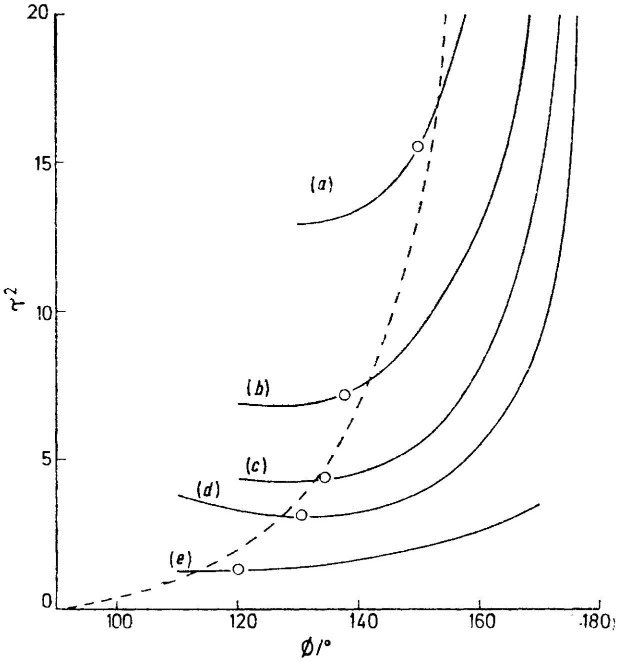

FIGURE 1 (——), Curves obtained by *ab-initio* UHF calculations for the radicals (*a*) N_3^{2-} (1.25), (*b*) NO_2 (1.2), (*c*) CO_2^- (1.26), (*d*) BO_2^{2-} (1.35), and (*e*) BF_2 (1.32). (Bond lengths, in Å, are given in parentheses); (○), *ab-initio* UHF calculations of minimum energy for each radical; (– – – –), curve obtained from equation (1)

RESULTS

Our major results are summarised in Figure 1, in which calculated τ^2 values are plotted against ϕ (bond lengths given in brackets). In order to calculate τ the experimentalist's procedure was used; that is, the calculated A and $2B$ values were divided by A^0 and $2B^0$ for the respective atoms to obtain C_s and C_p. This obviates the difficulty of extracting C_s and C_p from the molecular orbitals which include atomic-orbital overlap. The similarity of the curves in Figure 1 to those obtained by Owens [6] shows that both procedures lead to qualitatively similar results. Since this similarity exists there is no need to discuss the more approximate INDO calculations in depth.[6]

DISCUSSION

Major Conclusions.—The plots in Figure 1 represent a series of ϕ against τ^2 curves for individual molecules. The fact that these 'individual' curves do not fit equation (1) is the reason why Owens rejected the equation. However, equation (1) was meant to be quite general and it was not only inappropriate but unnecessary to use a minimum-energy criterion in its derivation. In contrast, INDO and *ab-initio* calculations are molecule dependent and use a minimum-energy criterion. We contend, therefore, that each 'individual' curve provides only one physically significant point that should come close to falling on the curve predicted by equation (1), namely that for the equilibrium bond angle (○ in Figure 1). It can be seen that such points, for this series of isoelectronic molecules, fall remarkably close to the curve for equation (1). Once these conclusions are accepted there is no need to discuss the accuracy of the INDO or *ab-initio* calculations for non-equilibrium geometries, or whether an environment surrounding the molecule will alter the 'individual' curves. It should be further emphasised that any criticism as to how the curves were obtained applies equally well to the INDO method.

The most reliable calculations are those at the energy minimum, that is at optimum bond length and bond angle, because our test of wavefunctions with real molecules exists only in this region. The points of minimum energy on these curves, noting that the bond lengths have been chosen rather than optimised with respect to the total energy, lie remarkably close to the curve for equation (1). The chosen bond lengths are thought to be close to their optimum at the optimum bond angle and therefore these points of minimum energy on each curve correspond closely to real radicals. To check on this the bond lengths in CO_2^- were varied. The results are in Figure 2. It is clear that for bond lengths up to at least the optimum the results follow equation (1) well. As noted before, the reliability of the calculations as the molecule starts to dissociate must

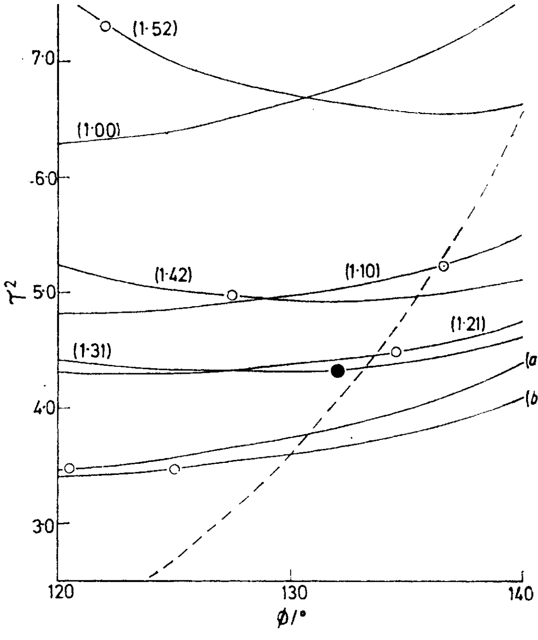

FIGURE 2 (——), Curves obtained from *ab-initio* UHF calculations for the CO_2^- radical for the bond lengths (in Å) shown in parentheses; (○), *ab-initio* UHF calculations of minimum energy for each curve; (●), the calculation of lowest energy. Curves were also obtained from *ab-initio* UHF calculations for the CO_2^- bond length (1.26 Å) in the field of (*a*) a unit positive charge placed 1.6 Å from the C atom on an axis bisecting the two oxygen atoms, (*b*) a positive charge of 10 units placed similarly 8 Å from the C atom. (– – – –), Curve obtained from equation (1) be considered. The $\langle S^2 \rangle$ value increases rapidly for CO_2^- above the optimum bond length, in itself indicative of dissociation. Spin contamination is not responsible for the deviations from equation (1) for CO_2^- since configuration-interaction calculations including all the single and necessary double excitations parallel the behaviour of the UHF calculations.

It is not our concern whether or not Coulson intended his derivations to be applicable to hypothetical molecules, such as molecules far removed from their equilibrium geometries. Our results do show however that real molecules follow equation (1) remarkably well.

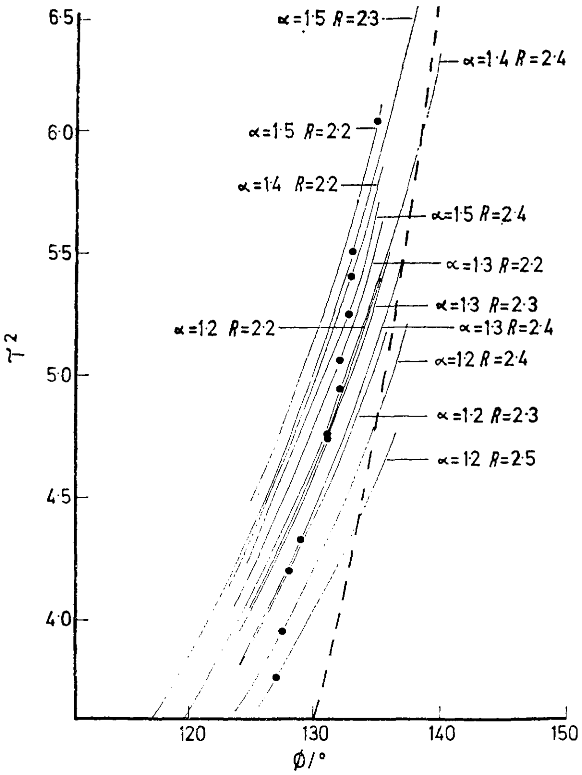

FIGURE 3 *Ab-initio* UHF calculations on the BH_2 radical for various bond lengths (R/a.u.) and exponents (α) of the hydrogen-like atomic orbital: The filled circles correspond to the calculations of lowest energy on each curve; the broken line is obtained from equation (1)

The Neutral Radical BH_2.—This radical contains only seven electrons and is therefore not directly comparable with the remaining radicals. However, the possibility of changing the hydrogen-orbital exponent as well as the bond length gives a further variable against which the qualitative validity of equation (1) can be tested. Using a minimal basis set it was also feasible to carry out configuration-interaction calculations which include all the excited configurations. In Figure 3 the UHF results are used to plot τ^2 against ϕ. The line through the points of minimum energy on each curve accurately parallels that of equation (1), again indicating that the equation is valid qualitatively. The agreement would be quantitative if $A^0/2B^0$ for boron is multiplied by *ca.* 0.8 because of orbital changes on molecule formation.

It is also probable that the basis set of orbitals used does not reproduce the ' experimental ' value of $A^0/2B^0$ for the boron atom. We decided to evaluate the theoretical $A^0/2B^0$ in the following simple way. A complete configuration-interaction calculation (only 15 configurations are included in the doublet spin-state ground state) of the boron atom, using a minimal basis set of atomic orbitals as before, in the field of two unit positive charges, simulating the BH_2 molecule with $X = 1.2$, $\phi = 125°$, and $R(B-H) = 2.6$ a.u.* Since the orbitals on the protons are not included there are no overlap problems and τ^2 can be evaluated from C_p^2/C_s^2. Since this quantity should be the same as $A/2B$, the ' theoretical ' $A^0/2B^0$ can be found. Whereas the value $A^0/2B^0 = 19.02$ was used for the radicals containing boron in both Figures 1 and 3, the ' calculated ' value is 17.5. This is in the right direction to bring the BH_2 ' theoretical ' τ^2 values closer to that predicted by equation (1).

If the unit positive charges are replaced by positive charges of two atomic units, $A/2B$ must be multiplied by a theoretical value of $A^0/2B^0 = 23.4$ to reproduce C_p^2/C_s^2 from the molecular orbital. This is no doubt an extreme calculation to simulate the BF_2 or BO_2^{2-} radicals but it is predicted that the larger is the electronegativity of Y in a radical XY_2 the larger $A^0/2B^0$ should be. This is consistent with the theoretical BH_2 results lying above, and the BF_2 and BO_2^{2-} results lying below, the curve of equation (1).

Medium effects. It could perhaps be argued that, for real systems, e.s.r. parameters often pertain to molecules or ions in perturbing media and that it may be better to use the separate molecular curves in Figure 1 instead of equation (1). Such perturbations have been extensively studied, and do indeed modify the e.s.r. parameters for ions, although they are probably insignificant for neutral radicals. (Obviously from an experimental point of view, care must be taken to ensure that librations or restricted rotations are not partially averaging the anisotropic parameter.) However, we can be certain that the theoretical curves for each radical in Figure 1 should not be used to reproduce environmental effects since the corresponding Hamiltonian operator in these calculations did not contain any terms to represent the lattice interactions. These interactions take the form of crystal fields that modify electron distributions rather than acting as steric constraints that simply change the geometries of radicals.

In order to probe this situation further, by way of demonstration rather than as a comprehensive study, we used a simple ion-pair model, CO_2^-–Na^+ where the Na^+ was represented by a point charge (Figure 2). The results show that a different curve for the CO_2^- radical must be drawn for each situation. It serves no useful purpose to simulate actual environments when equation (1) provides the necessary qualitative information.

Comparison with experiment. Unfortunately, to our

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* 1 a.u. = 0.529 16 Å.

knowledge the bond angle ϕ has only been unequivocally determined by other experimental methods for one radical, namely NO_2. In this case, however, the bond angle calculated using τ^2, as obtained from A and $2B$ and equation (1), is almost equal to the experimental angle, which strongly supports our conclusion that equation (1) serves a useful purpose.

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