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Electronic Structure of Unstable Intermediates

V. The Electronic Structure of the Closed-Shell Intermediate HBO

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The geometry of the linear molecule HBO, has been investigated within the restricted Hartree-Fock LCAO-MO-SCF approximation. The calculated bond lengths for the near Hartree-Fock calculation were $R(\text{H–B}) = 2.1913$ bohr, $R(\text{B–O}) = 2.2284$ bohr. Several one electron properties have been calculated for the minimum energy configuration.

Key words: HBO, electronic structure of ~

1. Introduction

This paper presents the results of an *ab-initio* LCAO-MO-SCF investigation of the reactive intermediate HBO, which has recently been detected experimentally by Porter and Lory [1]. Theoretical calculations on unstable intermediates can give useful information on the structure and bonding of such species [2], and for linear HBO we have computed the equilibrium bond lengths and several one electron properties, following our earlier work on similar triatomic molecules [3–5]. Although there have been no previous calculations on the neutral species HBO, the anion, HBO^-, which has been shown to be bent by observation of its E.S.R. spectrum [6], has been studied theoretically by Claxton [7], using the Unrestricted Hartree-Fock method.

2. Method of Calculation and Basis Sets

Calculations were performed on an IBM 370/195, using the programme ALCHEMY [8]. An estimate of the minimum energy and corresponding bond lengths was obtained by a least-squares fit of a quadratic function of the bond length to the total energy.

The basis sets were of DZ + P and BA + P quality, and details can be found in our earlier work [3–5]. The polarization function exponents were taken from similar quality calculations on HCN (for the H atom exponents) and on BF and CO (for the B and O exponents respectively) [9].

In the light of previous work [3–5], the basis sets are sufficiently large that further optimisation of the polarization function exponents would make little difference to the results.

Table 1. Valence orbital energies for HBO and HCN calculated with the BA + P basis set (values in hartree)

Orbital	Molecule	
	HBO	HCN
3σ	-1.3379	-1.2543
4σ	-0.6736	-0.8244
5σ	-0.6211	-0.5810
1π	-0.5253	-0.5089
2π[b]	$+0.0188$	$+0.1457$

[a] Reference [9].
[b] Virtual orbital.

3. Results

Calculations were carried out for various values of R(H–B) and R(B–O) for each basis set (full details are available from the author).

The minimum energy obtained for the DZ + P basis was -100.20126 hartree, with $R(\text{H–B}) = 2.228$ bohr, $R(\text{B–O}) = 2.225$ bohr and Virial Ratio $= -2.00013$. For the larger BA + P basis set, the corresponding values of $E = -100.20870$ hartree, $R(\text{H–B}) = 2.1913$ bohr, $R(\text{B–O}) = 2.2284$ bohr and Virial $= 1.99986$ were obtained. The computed energies for the ions HBO^+ and HBO^- at the latter bond lengths were $E^+ = -99.77242$ hartree and $E^- = -100.18900$ hartree, and the vertical ionization potential for HBO calculated to be 0.44 hartree compares with the Koopman's theorem value of 0.52 hartree. The valence orbital energies are compared with those for HCN in the case of the BA + P basis in Table 1. There is as yet no photo-electron spectra available for this molecule, but the first IP should be from the 1π orbital.

4. Discussion

The deviation of the atomic energies from the Hartree-Fock limit with the BA + P basis set is approximately 0.0002 hartree, and we can conclude that the energy as computed is within ~ 0.005 hartree of the Hartree-Fock limit [10]. Furthermore, the difference between the total energy as given by the wavefunction and the sum of the atomic energies using the same basis gives the contribution to the dissociation energy for a wavefunction with this basis.

The atomic energies of boron and oxygen using the BA + P basis are: boron (^2P state) -24.52906 hartree; oxygen (^3P state) -74.80938 hartree [9]. For the relevant value for the energy of the hydrogen atom, an *ab initio* calculation was performed, with the ATSCF programme [11], using the same basis as in the molecular calculations. The energy obtained was -0.49999 hartree.

Since the sum of the atomic energies is -99.83843 hartree, the difference between this and the calculated molecular energy of -100.20870 hartree is 0.37027 hartree. (The Hartree-Fock contribution to the dissociation energy would be expected to be about 0.005 hartree larger [3].) The energies of the boron and oxygen atoms for the DZ basis are: boron -24.5279 hartree (for the ^2P

Table 2. Population analysis for the BA + P basis set for valence orbitals of HBO

Orbital	BA + P		
	G_H[a]	G_B	G_O
3σ	0.01	0.33	1.66
4σ	0.80	0.76	0.44
5σ	0.28	0.35	1.37
1π	−0.02	0.74	3.29
Total[b]	1.07	4.17	8.76

[a] Gross atomic populations.
[b] Including 1σ and 2σ orbitals.

state); oxygen −74.80418 hartree (for the ^3P state) [12]. The hydrogen basis set being the same in both DZ + P and BA + P calculations, the sum of the atomic energies for the DZ + P basis is −99.83206 hartree, and the calculated dissociation energy from the DZ + P wave function is therefore 0.37212 hartree, quite similar to the BA + P value. Both basis sets give bond lengths shorter than those estimated by Porter and Lory [1], with only the BA + P basis agreeing with them that the B–O bond length is the longer.

By comparison with an *ab initio* calculation on the isoelectronic molecule HCN [9], the ground state configuration of HBO was taken to be:

$$1\sigma^2\, 2\sigma^2\, 3\sigma^2\, 4\sigma^2\, 5\sigma^2\, 1\pi^4 \quad {}^1\Sigma^+ .$$

The nature of bonding was examined with the usual Mulliken population analysis [13]. There are small differences between the results for the two basis sets but the main conclusions are the same, and we discuss only the BA + P results (Table 2). The pattern of the valence orbitals is comparable to that for HCN: 3σ is a sigma bond, boron to oxygen, made up of *s*-orbitals on oxygen and *sp* on boron. 4σ is a sigma bond, hydrogen to boron, of *s* character on hydrogen, *sp* on boron. The 5σ orbital is mainly a $2p$ lone pair on oxygen. The pi valence orbital is a boron-oxygen pi bond, with substantial polarization towards oxygen. The polarization functions have an appreciable population in all the valence orbitals. For the pi orbital, however, the population analysis suggests a different interpretation of their character. Comparing their population in the BA + P approximation to that in the DZ + P, there is a marked reduction. This difference may be attributed to a superior description of the pi symmetry orbitals in the BA + P case, as the number of functions on boron and on oxygen is double that for the DZ basis. It seems likely that the basis set for the pi symmetry orbitals on boron and oxygen is insufficient for an adequate description of the bonding. That the hydrogen pi symmetry basis functions are unaltered between the basis sets does not affect the argument, as the total population on hydrogen is small. The population analysis can be summarised as indicating a formulation of the species as:

$$\mathrm{H{-}B{=}O}\colon\ \delta^+\,\delta^- .$$

Table 3. Values of one-electron properties, calculated at optimum geometry, (R(H–B) = 2.1913, R(B–O) = 2.2284), with BA + P basis

Property	Value	
	Atomic units	CGS units
Neutral HBO		
Dipole moment (Debye)	– 1.2831	– 3.2612 D
Quadrupole moment		
H	–17.3343	–23.3129 barn
B	– 6.0874	– 8.1870 barn
O	4.3422	– 5.8399 barn
Field gradient		
H	0.6726	—
B	0.4311	—
O	– 1.7505	—
Force on nucleus		
H	0.01335	—
B	– 0.01192	—
O	– 0.01902	—
Quadrupole coupling constant		
^{2}H	0.6576×10^{-10}	4.3269×10^{-1} MHz
Force constants		
H–B	0.2760	4.2967×10^6 dyne cm^{-1}
B–O	10.045	15.538×10^6 dyne cm^{-1}

One further interesting feature of the population analysis is the fact that the boron is electron deficient to the extent of almost one unit of charge for the neutral species. For the cation, this is further increased with most of the overall positive charge centered on boron, there remaining some negative charge excess on the oxygen centre. On adding an electron to the neutral species, the electron-deficiency is cancelled, with the overall charge of the molecule being resident mostly on the oxygen atom.

The one electron properties given in Table 3 have been calculated as in a previous paper in this series [5], using formulae given in papers of McLean and Yoshimine [14, 15]. The quadrupole coupling constant for ^{2}H was derived by use of the experimental value of 2.738×10^{-27} cm^2 for the nuclear electric quadrupole moment, given by Ramsay [16].

Force constants for bond vibrations were calculated by the curve-fitting method outlined in a previous paper [5]. The values for these quoted by Porter and Lory [1] are: 4.27 and 13.86 dyne cm^{-1}, for H–B and B–O respectively. Our results of 4.2967 and 15.538 dyne cm^{-1}, for the same respective bonds, are in tolerable agreement: being shorter bond lengths, larger force constants are expected. The high electron deficiency obtained for the boron may account for the difficulty of observing this molecule compared with its trimer, boroxine. It is hoped this work will stimulate further experimental measurements on this species.

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