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Relationes

Structure and Magnetic Properties of Some Boron Containing Radicals: A Molecular Orbital Study

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Equilibrium geometries, hyperfine coupling constants and g-tensors have been calculated for seven boron containing free radicals using the INDO method. *Ab initio* calculations are reported for BO and BS.

Key word: Boron containing radicals

1. Introduction

The INDO method has been extensively applied to free radicals containing the first row elements C, N, O, and F but boron has, as yet, received little attention. A fair number of small boron-containing oddelectron species are now known and we report a systematic study of their geometries, isotropic hyperfine coupling constants and g-tensors within the INDO approximations. Minimisation of the total energy with respect to all geometrical parameters was performed for BO, BS, BH_2, BF_2, and BH_3^- and partial optimisation for $\dot{C}H_2BMe_2$ and BMe_3^-.

2. Calculations

The INDO program, calculation of isotropic hyperfine coupling constants, and method of geometry optimisation have been described previously [1, 2]. The g-tensors were evaluated from the INDO wavefunctions as outlined by Morikawa, and Someno [3]. *Ab initio* calculations were performed using the ATMOL program with both minimum basis sets of Slater type orbitals (STO-3G) and extended bases of double zeta functions.

Hyperfine coupling constants for ^{11}B were obtained using scaling factors of 674.74 G for *pre*-annihilation spin densities and 667.72 for *post*-annihilation. These values, resulting from a least squares fit of experimental coupling constants to the INDO B 2s spin densities, are comparable with the Hartree-Fock value of 720 G. The results are summarised in Tables 1–3.

Table 1. Results of INDO calculations on radicals containing boron

Radical	Geometry			Coupling constants (G)		
	Parameter	Exptl.	INDO	Nucleus	Exptl.	INDO
BO	R(BO)	1.204 Å	1.3 Å	^{11}B	366.8	349.6 (349.8)
BS	R(BS)	1.609 Å	1.63 Å	^{11}B	283.9	272.4 (171.9)
BH_2	R(BH)	1.18 Å	1.184 Å	^{11}B	—	162.7 (159.6)
	$\widehat{HBH}$	131°	129.3°	^{1}H	—	8.57 (10.97)
BF_2	R(BF)	—	1.442 Å	^{11}B	295.0	326.6 (323.2)
	$\widehat{FBF}$	—	118.0°	^{19}F	190.0	195.5 (198.1)
BH_3^-	R(BH)	—	1.212 Å	^{11}B	20.7	94.8 (88.13)
	$\widehat{HBH}$	—	115.4°	^{1}H	$-$ 15.1	$-$ 9.38 ($-$6.81)
BMe_3^-	R(BC)	—	1.553 Å	^{11}B	25.0	16.25 (10.7)
	$\widehat{CBC}$		120.0°	^{1}H	—	35.2 (44.1)
$\dot{C}H_2BMe_2$	$R(BC_{CH_2}$	—	1.495 Å	^{11}B	$-$ 4.0	$-$ 11.86 ($-$7.82)
(twisted)	$R(BC_{Me})$	—	1.536 Å	$^{1}H_{CH_2}$	$-$ 18.0	$-$ 17.53 ($-$16.85)
	$\widehat{HCB}$	—	124.2°	$^{1}H_{Me}$	4.3	1.46 (1.41)
	$\widehat{CBMe}$	—	118.7°			
(planar)	$R(BC_{CH_2})$	—	1.514	^{11}B	$-$ 4.0	$-$ 1.25 ($-$0.82)
	$R(BC_{Me})$	—	1.536	$^{1}H_{CH_2}$	$-$ 18.0	$-$ 15.92 ($-$15.31)
	$\widehat{HCB}$	—	125.2	$^{1}H_{Me}$	4.3	11.23 (13.95)
	$\widehat{CBMe}$	—	118.7			

Table 2. Results of *ab initio* calculations on BO and BS performed using experimental bond lengths; results after spin annihilation in brackets

	BO		BS	
	$a(^{11}B)/G$	$\langle S^2 \rangle$	$a(^{11}B)/G$	$\langle S^2 \rangle$
Minimum basis	254 (234)	1.027 (0.797)	197 (187)	0.933 (0.770)
Extended basis	310 (278)	0.847 (0.755)	250 (222)	0.894 (0.762)

Table 3. Calculated g-tensors for some boron radicals

	g_{zz}	g_{xx}	g_{yy}	$\bar{g}$
BO	2.0023	2.0013	2.0013	2.0016
BS	2.0023	2.0000	2.0000	2.0008
BF_2	2.0041	1.9996	2.0025	2.0021
BH_2	2.0023	1.9993	2.0023	2.0013
$\dot{C}H_2BH_2$	2.0023	2.0025	2.0024	2.0024

3. Discussion

3.1. BO *and* BS

The ESR spectra of BO [4] and BS [5] have been reported by Weltner and coworkers using matrix isolation techniques. The bond lengths, obtained from UV spectra, are 1.204 Å [6] and 1.609 Å [7]. The INDO calculation overestimates the BO bond length by 0.1 Å but gives better agreement for BS. The ^{11}B coupling constants are in reasonable accord with experiment, as are those obtained from the ATMOL calculations (Table 2). A feature of the latter is the large deviation from 0.75 found for the expectation value of S^2. Similar marked spin contamination has been found in *ab initio* UHF calculations on the isoelectronic CN radical [8]. However the INDO wavefunctions gave $\langle S^2 \rangle = 0.750$ for both BO and BS after a single spin annihilation.

It has been estimated that in a neon matrix [4] BO has $g_{\parallel} = 2.0012$ and $g_{\perp} = 2.0015$ with the shift in $g_{\parallel}$ from free spin attributed to a matrix effect. If $g_{\parallel}$ and $g_{\perp}$ were equally affected by the matrix, $g_{\perp} - g_{\parallel} = 0.0003$ should be comparable with our theoretical value, but we find -0.0010. The sign of the anisotropy is correctly predicted for BS where experimentally $g_{\parallel} = 2.0016$ and $g_{\perp} = 1.9941$.

3.2. BF_2

The radical has been observed trapped in a xenon matrix at 4 K. *Ab initio* RHF calculations using several different Gaussian basis sets [11] gave bond angles in the range 117°–120° and bond lengths in the range 1.32–1.39 Å. Our calculated coupling constants agree well with experiment and the bond angle seems reasonable; the B–F distance is probably overestimated. We predict a fairly substantial anisotropy in the g-tensor but only the isotropic value of 2.0012 has been experimentally determined.

3.3. BH_3^- *and* BMe_3^-

ESR spectra assigned to BH_3^- have been observed in the γ-irradiated borohydrides of potassium [12] and tetramethylammonium [13]. Differences between the two sets of results were attributed to strong environmental effects, but both investigations indicate a planar geometry. However *ab initio* UHF calculations predicted a pyramidal structure with an out-of-plane angle of 9° [14]. Claxton *et al.* [15] have also attempted to introduce environmental effects into *ab initio* calculations to see if the experimental results could be better accomodated. Our INDO calculation also predicts a pyramidal geometry (Table 1) with coupling constants in poor agreement with experiment. However, if the geometry is constrained to be planar, we estimate $a(^{11}B) = 33.3G$ and $a(^{1}H) = -18.9G$. The boron coupling is particularly sensitive to bending.

A poorly resolved 25G quartet observed in the γ-irradiated ammonia adduct of BMe_3 has been tentatively assigned to BMe_3^-, [16] although the absence of resolvable proton splitting was considered unusual. Our calculations predict a substantial methyl proton interaction and do not support the assignment to BMe_3^-.

3.4. $Me_2B\dot{C}H_2$ *and* CH_2BH_2

A poorly resolved ESR spectrum observed in γ-irradiated BMe_3 has been assigned to $\dot{C}H_2BMe_2$ with a methylene proton splitting of $-18G$, a ^{11}B splitting of $-4G$ and a methyl proton coupling of 4.3G [16]. We initially assumed a planar configuration for this radical but found that twisting the CH_2 group to a perpendicular position lowered the INDO energy by 21 kJ mol^{-1}: results for both geometries are given in Table 1. The level of agreement with the experimental hyperfine splittings is comparable for both geometries and does not permit a clearcut choice of conformation. We therefore investigated the properties of the simpler, but as yet unknown, radical, CH_2BH_2. The INDO method again gave a minimum energy geometry with the CH_2 and BH_2 groups planar and perpendicular to one another. However *ab initio* calculations using the same geometries placed the planar conformation 0.0177 a.u. lower in energy using a minimum basis and 0.0141 a.u. lower in energy using a double zeta basis. Although these calculations do not allow us to draw any firm conclusions about the preferred conformation, they do indicate that the barrier to internal rotation in such systems is low.

4. Conclusions

We have shown that the INDO method is capable of reproducing the geometries and spin properties of boron containing radicals in reasonable agreement with experiment; difficulties experienced with BH_3^- have also been encountered in *ab initio* studies. Discussion of our estimated *g*-tensors is hampered by a lack of experimental information and by uncertainty about the nature of matrix effects.

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