

Electronic-structure calculations for BC radical by density-functional theory

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The electronic structure of BC radical has been calculated using the density-functional theory with a gradient-corrected local-spin-density approximation. The calculated results for the ground state are as follows: The bond length is 1.497 Å. The harmonic frequency is 1151 cm⁻¹. The atomization energy is 4.856 eV. The electric dipole moment is -1.114 Debye (B⁺C⁻). The isotropic and anisotropic hyperfine coupling constants are 37.3 and 2.7 G for ¹¹B, respectively, and 3.4 and -2.2 G for ¹³C, respectively.

1. Introduction

The electronic structure of BC radical has been carried out using *ab initio* theories¹⁻⁶⁾. The BC in the ground state has the spin $\frac{3}{2}$. The equilibrium bond length r_e for the ground state was calculated to be 1.501 Å by Hirsch *et al.*³⁾, 1.491 Å by Oliphant *et al.*⁵⁾ and 1.495 Å by Martin *et al.*⁶⁾. These values are in good agreement with 1.491 Å observed by Fernando *et al.*⁷⁾.

The electric dipole moment calculated by Hirsch *et al.* was not a continuous function of the bond length and they had to determine the value of the dipole moment by resorting to graphical averaging³⁾. They obtained -0.788 Debye at $r_e = 1.501$ Å. The minus sign of the dipole moment means the polarization B⁺C⁻. Knight *et al.* obtained -0.725 Debye at $r_e = 1.521$ Å⁴⁾. Although these two values are in good agreement with each other, there is the question in the reliability of them.

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Knight *et al.* have observed the hyperfine coupling constants (HFCC's) for BC in neon, argon and krypton matrices by the electron spin resonance (ESR) measurements⁴⁾. The observed results depend on the matrices. They obtained $A_{\parallel}({}^{11}\text{B}) = +35.7$ G, $A_{\perp}({}^{11}\text{B}) = +28.2$ G, $A_{\parallel}({}^{13}\text{C}) = +1.8$ G and $A_{\perp}({}^{13}\text{C}) = +5.4$ G for BC in neon matrix at 4K⁴⁾. Here, A_{\parallel} and A_{\perp} are the parallel and perpendicular components of the A tensor. *The signs of the observed A -values were determined from the comparison with the results calculated for BC with $r_e = 1.521$ Å⁴⁾.*

The HFCC's are sensitive to geometry. The difference between r_e used in the calculation (1.521 Å) and the observed one (1.491 Å) is 0.030 Å. Consequently, in order to clarify the signs of the overved A -values, it is necessary to examine the bond-length dependence of the A -values. In addition, since the HFCC's are also sensitive to the treatment of the electron correlation, we must use the reliable method for its treatment.

The usefulness of the density-functional theory (DFT)^{8,9)} for the calculations of electronic structures of molecules, such as the total energy, the harmonic frequency, the electric dipole moment and so on, is well-established¹⁰⁾. Recently we calculated the isotropic HFCC's of radicals using the DFT with Slater-type-orbital (STO) basis set and confirmed its usefulness^{11–13)}. It is expected that the DFT yields the reliable electronic-structure of BC radical. In the present paper we report the results of the calculations for BC radical using the DFT with a gradient-corrected local-spin-density approximation (GC-LSDA) and the STO basis set.

2. Calculation method

The calculations have been carried out using the same method as those in Ref.13. We have employed the expression for homogeneous electron gas in the Hartree-Fock approximation plus Becke's gradient correction¹⁴⁾ as the exchange-energy functional and Vosko-Wilk-Nasair's expression¹⁵⁾ plus Perdew's gradient correction¹⁶⁾ as the correlation-energy functional in the present study. As the basis set for each of B and C atoms, we used three $1s$ -, three $2s$ -, fifteen ($= 5 \times 3$) $2p$ - and twenty ($= 4 \times 5$) $3d$ -type STO's¹³⁾.

3. Results and Discussion

The calculations were carried out for BC radical with seven spin-up and four spin-down electrons. The electronic structures of BC were calculated at eight points in the bond-length range between 1.46 and 1.53 Å.

(1) Equilibrium bond length (r_e)

The calculated total energies were fitted to a third-order polynomial of the bond length r using the least-squares method. We shall call the resulting function $E_{\text{tot}}(r)$. Then r_e is obtained as the solution of the following equations

$$\frac{dE_{\text{tot}}(r)}{dr} = 0 \quad \text{and} \quad \frac{d^2E_{\text{tot}}(r)}{dr^2} > 0$$

We obtained $r_e = 1.497$ Å. This is in fairly good agreement with the observed result (1.491 Å)⁷⁾ and the previously calculated ones (1.501³⁾, 1.491⁵⁾, 1.495 Å⁶⁾).

(2) Harmonic frequency (ω_e)

ω_e was calculated using the force constant k obtained from the following equation:

$$k = \left. \frac{d^2E_{\text{tot}}(r)}{dr^2} \right|_{r=r_e}$$

The result is $\omega_e = 1151$ cm⁻¹. This is in fairly good agreement with the previously calculated ones (1140³⁾ and 1147.9 ± 10 cm⁻¹ ⁶⁾).

(3) Atomization energy (D_0)

The calculated ground-state energy of BC with the spin $\frac{3}{2}$ is -1705.690 eV at $r_e = 1.497$ Å. On the other hand, those for B atom with the spin $\frac{1}{2}$ and C atom with the spin 1 are -670.812 and -1029.951 eV, respectively. Taking into account the zero-point energy $\frac{1}{2}\hbar\omega_e$, we obtain $D_0 = 4.856$ eV. Although this is slightly higher than the results calculated by Hirsch *et al.* (4.19 eV)³⁾ and Martin *et al.* (4.26 eV)⁶⁾, this is in good agreement with the result observed by Verhaegen *et al.* (4.6 ± 0.3 eV)¹⁷⁾.

(4) Electric dipole moment (μ)

The calculated μ -value increases monotonically from -1.158 to -1.080 Debye with an increase in the bond length from 1.46 to 1.53 Å. We obtained $\mu = -1.114$ Debye at $r_e = 1.497$ Å by the interpolation. Our result is greater than the previous ones^{3,4)} by 0.33 ~ 0.39 Debye in magnitude.

(5) Hyperfine coupling constants

For the BC radical the isotropic (a_{iso}) and anisotropic (B_{dip}) HFCC's are related to A_{\parallel} and A_{\perp} as follows.

$$A_{\parallel} = a_{\text{iso}} + 2B_{\text{dip}} \quad \text{and} \quad A_{\perp} = a_{\text{iso}} - B_{\text{dip}}.$$

Table 1 shows the HFCC's calculated for a free BC radical at $r_e = 1.497 \text{ \AA}$ together with the observed ones. The results calculated for the free BC radical are as a whole in good agreement with those observed for BC radicals trapped in neon and argon matrices at 4K. However, the sign of $A_{\parallel}({}^{13}\text{C})$ in our results is minus and is opposite to that determined by Knight *et al.*⁴⁾ as shown in Table 1.

Table 1 Hyperfine coupling constants (in G) of BC radical with spin $\frac{3}{2}$.

		Calculation (GC-LSDA) $r_e = 1.497 \text{ \AA}$	Experiment ^{a)} (ESR) in Ne in Ar	
${}^{11}\text{B}$	a_{iso}	37.3	30.7	
	B_{dip}	2.7	2.5	
	A_{\parallel} ^{b)}	42.7	35.7	
	A_{\perp} ^{c)}	34.6	28.2	30.0
${}^{13}\text{C}$	a_{iso}	3.4	4.2	
	B_{dip}	-2.2	-1.2	
	A_{\parallel} ^{b)}	-1.0	1.8	
	A_{\perp} ^{c)}	5.6	5.4	6.1

^{a)}Ref.4. ^{b)} $A_{\parallel} = a_{\text{iso}} + 2B_{\text{dip}}$. ^{c)} $A_{\perp} = a_{\text{iso}} - B_{\text{dip}}$.

With an increase in the bond length from 1.46 to 1.53 \AA , $a_{\text{iso}}({}^{11}\text{B})$, $B_{\text{dip}}({}^{11}\text{B})$, $a_{\text{iso}}({}^{13}\text{C})$ and $B_{\text{dip}}({}^{13}\text{C})$ change monotonically as follows.

$$\begin{aligned} a_{\text{iso}}({}^{11}\text{B}) &: 38.76 \longrightarrow 35.96 \text{ G} \\ B_{\text{dip}}({}^{11}\text{B}) &: 2.76 \longrightarrow 2.71 \text{ G} \\ a_{\text{iso}}({}^{13}\text{C}) &: 2.68 \longrightarrow 4.08 \text{ G} \end{aligned}$$

$$B_{\text{dip}}(^{13}\text{C}) : -2.22 \longrightarrow -2.11 \text{ G.}$$

Consequently, the calculated $A_{\parallel}(^{13}\text{C})$ increases monotonically from -1.76 to -0.14 G in this bond-length range. According to our calculated results, if we assign a minus sign to $A_{\parallel}(^{13}\text{C})$ observed in neon matrix at 4K (namely $A_{\parallel}(^{13}\text{C}) = -1.8$ G), we get $a_{\text{iso}}(^{13}\text{C}) = 3.0$ G and $B_{\text{dip}}(^{13}\text{C}) = -2.4$ G as the observed values. The agreement between these two values and our calculated results (3.4 and -2.2 G) shown in Table 1 is fairly good.

In order to compare the theoretical results with the observed ones in more detail, it is necessary to carry out the ESR measurements for BC radicals in gas phase since the observed results depend on the kind of the matrices in which BC radicals are trapped⁴⁾.

4. Conclusion

We calculated the electronic structures of BC radical with the spin $\frac{3}{2}$ using the DFT with the GC-LSDA and STO basis sets. The results are as follows: For the ground state, $r_e = 1.497$ Å, $\omega_e = 1151$ cm⁻¹, $D_0 = 4.856$ eV and $\mu = -1.114$ Debye. In addition, we obtained $a_{\text{iso}}(^{11}\text{B}) = 37.3$, $B_{\text{dip}}(^{11}\text{B}) = 2.7$, $a_{\text{iso}}(^{13}\text{C}) = 3.4$ and $B_{\text{dip}}(^{13}\text{C}) = -2.2$ G. Consequently, we get $A_{\parallel}(^{13}\text{C}) = -1.0$ G. From this result, we conclude that the sign of $A_{\parallel}(^{13}\text{C})$ observed for BC radicals by ESR is minus in contrast with the assignment by Knight *et al.*⁴⁾.

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