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Singlet–Triplet Separation in CBr_2

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Abstract: Using ab initio (with effective core potentials) electronic structure theory, the equilibrium geometry and singlet–triplet separation were determined for CBr_2. The triplet was computed by using a single-configuration SCF wave function, while the singlet state used a two-configuration MCSCF wave function. This model is based on previous work on CH_2 and is discussed in detail. The Br effective core potentials are compared to all electron calculations for CHBr and found to give very similar results. The bond angle of the singlet is in agreement with experiment, while the computed triplet bond angle is very different from experiment. The singlet was computed to be ~8 kcal/mol lower than the triplet.

Introduction

In a previous paper[1] we reported on the structure and energetics of several simple halogenated carbenes (CHF, CHCl, CHBr, CF_2, and CCl_2). At that time we noted that much work had been done on the reactions of CBr_2, but we were unable to investigate CBr_2 because of the size of the calculation. With the aid of effective core potentials, this problem is now tractable.

The structures of both the singlet and triplet have been determined by using electron diffraction.[3] The carbon–bromine bond distance was found to be 1.74 Å for both the singlet and triplet state. The singlet state was assigned a bond angle of ~114°, while the triplet state was assigned an angle of ~150°. CBr_2 has been assumed to be a ground-state singlet based on the failure to observe nonstereospecificity in the addition reactions to olefins.[4]

Theoretical Approach

In this work we used the same theoretical approach as used previously[1] which is based on previous work[5,6] on CH_2. The work on CH_2 suggests that reliable structures and a reasonable singlet–triplet separation for this molecule can be obtained by treating the $^3B_1$ as a single-determinant self-consistent field (SCF) wave function $1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1\ 1b_1$; $^3B_1$, while the $^1A_1$ state is treated with a two-configuration MCSCF calculation, $c_1\ 1a_1^2\ 2a_1^2\ 1b_2^2\ 3a^2 + c_2\ 1a_1^2\ 2a_1^2\ 1b_2^2\ 1b_1^2\ (^1A_1)$. The near-Hartree–Fock limit calculation of Meadows and Schaefer[7] yields a separation of 10.9 kcal/mol with the use of this treatment. This is in excellent agreement with the accurate CI result of 10.6 kcal/mol obtained by Bauschlicher and Shavitt.[6] Based on error analysis they concluded a singlet–triplet separation of ~9.0 kcal/mol, which is in agreement with the determination of Lengel and Zare[8] and the large number of chemical determinations.[9-13] The previous work also showed good agreement between the limited experimental geometry information and our computed results.

Table I. Comparison of All-Electron vs. Valence Electron Calculation for CHBr[a]

	singlet		triplet			
	all	valence	all	valence	all	valence
		DZ				
RCH	1.103	1.105	1.075	1.075		
RCBr	1.972	1.961	1.891	1.888		
∠	102.6	102.0	125.6	124.8		
separation					12.4	10.1
C 2s population	1.83	1.85	1.48	1.50		
C 2p population	2.30	2.28	2.71	2.75		
		DZ + d				
separation					1.1	0.1

[a] The bond lengths are in Å and the separations are in kcal/mol, with a positive sign indicating the triplet being lower.

The all-electron basis sets use Dunning's double ζ (DZ) contractions. The hydrogen basis uses his (4s/2s) contraction[14] of Huzinaga's primitive set[15] (with a scale factor of 1.2); for carbon we used the (9s5p/4s2p) contraction[14] of Huzinaga's primitive set,[15] for chlorine the (12s9p/6s4p) contraction[16] of Veillard's primitive set,[17] and for bromine Dunning's (14s11p5d/8s6p2d) contraction of his own primitive set.[18] (This basis set was tabulated in our previous paper.[1]) The valence electron basis sets and effective core potential parameters are taken from Kahn et al.[19] The 3s and 3p Gaussian basis functions were not contracted, producing a valence basis (3s3p/3s3p) for Cl and bromine. For Br we used Kahn's 11-term fit to the effective core potentials, while for Cl we used Kahn's 9-term fit.

As we noted in our previous paper the addition of d polarization functions to carbon was needed to obtain a reasonable singlet–triplet separation, while the addition of polarization functions to the substituents had little effect on the singlet–triplet separation. The DZ + d basis starts from the DZ basis and adds a d function to the carbon. Based upon the trends observed in our previous calculations on halogenated carbenes,[1] a d exponent of $\alpha = 0.4$ was used. We also noted that the C–Cl bond length in CHCl $^1A'$ was too long by 0.07 Å. We attributed this to the lack of d functions on Cl. In order to improve the bond lengths a DZ plus polarization (DZP) was also used. This basis set starts with the DZ basis and adds d functions to both C and Br. Both d exponents were $\alpha = 0.4$.

Effective Core Potential Tests

In order to evaluate the use of effective core potentials (ECP) some tests were run comparing the valence electron with the all-electron calculations. At the CCl_2 DZ computed geometries, the singlet–triplet separation of −2.00 kcal/mol compared to the −2.9 kcal/mol value obtained with the all-electron DZ basis set.

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Table **II.** Summary of CBr_2 Calculations[a]

molecule	basis	S–T separation, kcal/mol	triplet R(CX)	triplet θ	triplet E	singlet R(CX)	singlet θ	singlet E
CBr_2	DZ	1.2	1.888	127.4	−64.52528	1.958	110.6	−64.52335
	DZ + d	−7.7	1.888[d]	127.4[d]	−64.55717	1.958[d]	110.6[d]	−64.56944
	DZP	−8.6	1.844	127.3	−64.57832	1.875	110.1	−64.59194
exptl[b]			1.74	~150		1.74	~114	
carbon 2s population[c]			1.59			1.93		
carbon 2p population			2.64			2.15		
total carbon population			6.22			6.08		

[a] Bond length is in Å and total energy is in hartrees. A negative sign for the singlet–triplet separation (S–T) indicates that the singlet is lower. [b] Reference 3. [c] Populations taken from DZ basis. [d] DZ geometry used.

Table **III.** Summary of Computed Equilibrium Geometries and Singlet–Triplet Separation[a]

	triplet R(CH)	triplet R(CX)	triplet θ	singlet R(CH)	singlet R(CX)	singlet θ	Δ
CH_2	1.075		128.8	1.106		102.5	12.8
CHBr	1.075	1.891	125.6	1.103	1.972	102.6	1.1
CHCl	1.075	1.735	123.3	1.101	1.762	102.0	−1.6
CHF	1.077	1.321	120.4	1.111	1.325	102.2	−9.2
CBr_2		1.844	127.3		1.875	110.1	−7.7
CCl_2		1.730	125.5		1.756	109.2	−13.5
CF_2		1.311	117.8		1.305	104.3	−44.5

[a] The bond lengths are in Å and the bond angle in degrees. The separations are in kcal/mol, where a positive sign indicates that the triplet is lower. All calculations except CHBr and CBr_2 represent optimizations at the DZ + d level. CHBr is optimized at the DZ level and CBr_2 at the DZP level.

More extensive tests were run for CHBr and are summarized in Table I. The bond length and angles are in good agreement and the singlet–triplet separation is in error by a maximum of 2.3 kcal/mol. The carbon Mulliken polulations computed by using ECPs are in agreement with those computed in the all-electron calculation. We should note that the singlet–triplet separation in CH_2 at the DZ + d level is 12.8 kcal/mol vs. about 9 kcal/mol for the best estimates. The use of effective core potential appears to introduce about an additional 2 kcal/mol error to this model.

Results and Discussion

The geometry was optimized for both the DZ and DZP basis. Using the optimum geometry computed with the DZ basis, we evaluated the singlet–triplet separation with the DZ + d basis. The results of these calculations are summarized in Table II and along with the previous work in Table III.

We compute the singlet to be 7.7 kcal/mol lower than the triplet at the DZ + d level and 8.6 kcal/mol lower with the DZP basis. This difference between the DZ + d and DZP is small and of about the same size as for CH_2 and CF_2. This small difference is additional support for our previous calculations which used only a DZ + d basis.

As noted above, this method treats the triplet better than the singlet by ~3 kcal/mol for CH_2, but the effective core potentials favor the singlet. Since these errors are of about the same magnitude and in opposite directions the singlet–triplet separation is probably very reasonable, but at this level of calculations not definitive.

Our previous explanation[1] was based on the destabilization of the triplet by electron-withdrawing substituents. Harrison et al.[20] have made a similar observation for some related compounds. As expected for the less electronegative Br, CBr_2 has a smaller singlet–triplet separation than CCl_2; however, the substitution of Br for Cl in both CHCl and CCl_2 causes only a small change in the splitting. The Mulliken populations show that in CBr_2, like the other halogenated carbenes, the singlet state arises from a unhybridized carbon atom, while the triplet state arises from an sp^2 (with an additional singly occupied out of the plane p) hybridized carbon. The total carbon Mulliken population is greater for the triplet state. This was true for all our previously studied halogenated carbenes, except CF_2.

The bond lengths at the DZP level are shorter than the DZ, the singlet shortening by 0.08 Å. At the DZP level, the singlet and triplet bond lengths are very similar, but both are ~0.1 Å longer than the experimental[3] result of 1.74 Å, which is 0.2 Å shorter than the C–Br experimental bond length in CH_3Br.[21] For CH_3Br the computed[22] bond length at the DZ–SCF level is 0.04 Å too long. If Cl is substituted for Br, the shortening going from CH_3Cl (1.781 Å)[21] to CHCl (1.689 Å)[23] is 0.09 Å. The difference in bond length for CBr_2 is attributed to the limited basis set, the use of effective core potentials, and any experimental uncertainty.

The singlet bond angle is in good agreement with experiment, both being ~112°. The triplet bond angles differ greatly: the computed value of 127° is 23° smaller than the experimental result of ~150°. This difference is far larger than can reasonably be expected. One possible explanation for the large $^3B_1$ angle is a result of observing vibrationally excited CBr_2. At the SCF level CBr_2 $^3B_1$ has a barrier of ~10 000 cm^{-1}; for CH_2 the barrier was reduced by ~30% at the CI level.[6] Therefore, the higher vibrational levels of CBr_2 would appear linear. The experiment obtains the geometry for the weighted average of all populated levels, so the formation of vibrationally excited CBr_2 molecules would make the bond angle appear larger. We should also note that the interpretation of the experiments is not always simple. In a previous study on $BrCCl_3$[24] there was some uncertainty as to the molecules present and an incomplete explanation for the long C–Br bond. One explanation for the long C–Br bond length was the presence of excited states. While we are unable to completely resolve the difference between our calculations and experiments, we feel that our $^3B_1$ bond angle of 127° is more accurate than the ~150° of the experiment. This is based on the fact that a bond angle of 127° is consistent with the trends observed in our calculations of CH_2, CF_2, and CCl_2 and the normal uncertainties associated with SCF geometry predictions.[25]

Conclusions

Calculations show CBr_2 to be a ground-state singlet in agreement with assumptions based on experimental data. The singlet bond angle is in agreement with electron-diffraction studies, while the triplet bond angle is very different from experiment. One possible explanation for this difference is the presence in the experiment of vibrationally excited $^3B_1$ CBr_2.

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