

Prediction of an Inverse Heavy-Atom Effect in H–C–CH₂Br: Bromine Substituent as a π Acceptor

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A comparison of spin–orbit coupling (SOC) calculated [CASSCF-(6,6)/(cc-pVDZ on C,H and VDZ+P on Br)] for bromomethylcarbene (**1**) and methylcarbene (**2**) predicts an unusual inverse heavy-atom effect by the Br substituent, particularly at geometries near the syn conformation. This is due to a vacant 4d orbital on the Br atom acting as a weak π -electron acceptor and overwhelming the even weaker effect of the π -symmetry lone pair donor 4p orbital, which in itself would cause a small normal heavy-atom effect.

The photophysical and photochemical term “heavy-atom effect” (more correctly, atomic-number effect)² refers to the influence of a substituent atom on molecular SOC that is caused by its large atomic number Z . Ordinarily, SOC is increased (normal heavy atom effect), because the atomic SOC constant ζ is approximately proportional to Z^4 and this magnifies contributions by a high- Z atom. A decrease in SOC upon introduction of a high- Z atom (inverse heavy-atom effect) in an organic molecule is rarely observed, and the first instance of decreased intersystem crossing rates upon introduction of a bromine substituent was greeted with puzzlement.³ In transition-metal complexes, the opportunities for inverse heavy-atom effects are recognized, and a qualitative rationalization has been based on noting that SOC is a square of a sum of signed atomic contributions.⁴ An inverse effect has been calculated at some internuclear separations in the diatomic, NeB.⁵

For SOC between a singlet (S) and a triplet (T) state, of particular importance in organic molecules, the addition of atomic contributions to SOC can be viewed as vectorial:⁶ if population equilibration among the T_x , T_y , and T_z sublevels is rapid, SOC is the length of a vector \mathbf{SOC} whose coordinates are the contributions provided by the sublevels: $|\mathbf{SOC}| = (|\langle T_x | H^{SO} | S \rangle|^2 + |\langle T_y | H^{SO} | S \rangle|^2 + |\langle T_z | H^{SO} | S \rangle|^2)^{1/2}$. When the vector \mathbf{SOC}_κ contributed to \mathbf{SOC} by a heavy atom κ of a substituent is comparable in length to the sum $\sum_\lambda \mathbf{SOC}_\lambda$ of vectors provided by all other atoms λ already present in the molecule, the final vector $\mathbf{SOC} = \mathbf{SOC}_\kappa + \sum_\lambda \mathbf{SOC}_\lambda$ will be longer than the original vector if \mathbf{SOC}_κ and $\sum_\lambda \mathbf{SOC}_\lambda$ are approximately parallel (normal heavy-atom effect) and shorter if they are approximately antiparallel (inverse effect). In a simple model for biradicals, the direction of each atomic contribution \mathbf{SOC}_λ to the coupling of the S_0 and T_1 states is dictated by the orientation and phase of contributions from pairs of natural atomic hybrid orbitals (NHOs) at atom λ to the two singly occupied orbitals (A,B) of the triplet.^{6,7}

The solid (**1**, $\kappa = \text{Br}$) and broken (**2**, $\kappa = \text{H}$) bold red lines in Figure 1 show $|\mathbf{SOC}|$ for S_0 – T_1 coupling computed as a function of the HCCX dihedral angle ω at geometries optimized for T_1 . The directions of the magnetic axes deduced from the spin–spin dipolar coupling tensor calculated as a function of ω are nearly the same

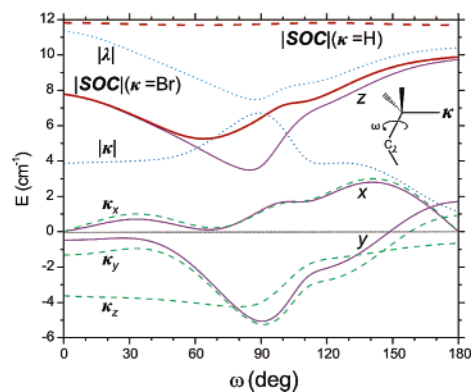


Figure 1. Bromomethylcarbene **1** ($\kappa = \text{Br}$): dihedral angle (ω) dependence of $|\mathbf{SOC}|$ (full red line) and the atomic contributions from the divalent carbon, $|\lambda|$ and bromine, $|\kappa|$ (dotted blue lines). The vector \mathbf{SOC}_λ is directed almost exactly along z ; the broken thin green lines κ_x , κ_y , κ_z show the three coordinates of \mathbf{SOC}_κ , and the full thin violet lines x , y , z show the three coordinates of the total spin–orbit vector \mathbf{SOC} . Methylcarbene **2** ($\kappa = \text{H}$): $|\mathbf{SOC}|$ is shown as a dashed red line.

in **1** and **2**, with x roughly perpendicular to the HCC plane and y nearly bisecting the HCC angle, as are the principal values (**1**, $D = 0.74$ – 0.82 and $E = -0.04$ – 0.06 cm^{-1} ; **2**, $D = 0.85$, $E = -0.04$; the S_0 – T_1 gap is large, and the effect of SOC on the calculated D and E values is below 0.01 cm^{-1}). For **2**, $|\mathbf{SOC}|$ is conformation-independent and similar to those calculated for other simple carbenes.^{7–9} As usual, it is dominated by a large z -directed contribution from the divalent carbon atom C_λ , where the two singly occupied orbitals of the triplet are largely localized.

Contrary to standard expectations, $|\mathbf{SOC}|$ is smaller for **1** than for **2** at all dihedral angles (Figure 1). This does not in itself demonstrate that the bromine substituent κ reduces $|\mathbf{SOC}|$ by its heavy-atom effect, since it could merely be its electronic effect that is reducing the contribution \mathbf{SOC}_λ provided by C_λ , as found previously⁹ in other substituted carbenes. Indeed, in **1** the bromine substituent does reduce \mathbf{SOC}_λ somewhat by decreasing the amplitude of orbitals A and B on C_λ due to their hyperconjugative delocalization into the CBr antibond, causing a dip in the total $|\mathbf{SOC}|$ near 90° . The dotted blue lines in Figure 1 clearly show a drop in $|\mathbf{SOC}_\lambda|$ and the associated increase in $|\mathbf{SOC}_\kappa|$.

However, the bulk of the reduction in $|\mathbf{SOC}|$ due to the Br substituent represents a true inverse heavy-atom effect. At all angles ω the Br atom makes an important negative contribution to $|\mathbf{SOC}|$ through its atomic contribution \mathbf{SOC}_κ , which is approximately directed along $-z$, opposite to the z -directed contribution \mathbf{SOC}_λ provided by C_λ (Figures 2 and 3). The reduction in $|\mathbf{SOC}|$ due to \mathbf{SOC}_κ is $\sim 35\%$ near syn and $\sim 17\%$ near anti geometries. To our

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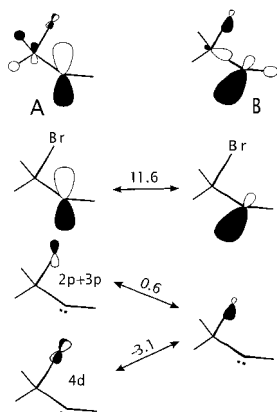


Figure 2. Singly occupied triplet orbitals *A, B* of bromomethylcarbene **1** in the syn conformation and the main contributions of NHO pairs to $|SOC|$ (in cm^{-1}).

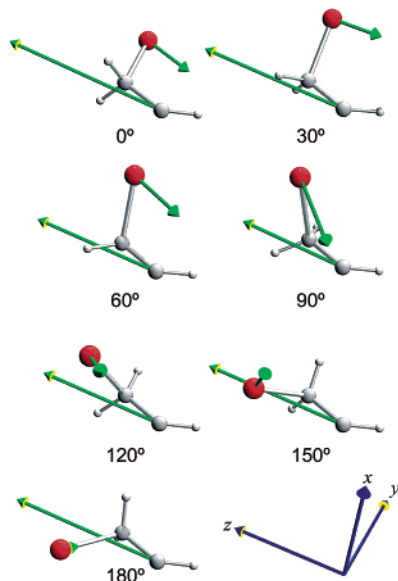


Figure 3. Bromomethylcarbene **1**: dihedral angle (ω) dependence of the SOC_λ and SOC_κ vectors in the principal axes of the magnetic dipole-dipole interaction tensor (x, y, z).

knowledge these results represent the first computational demonstration of an inverse heavy-atom effect in an organic molecule.

Why are the SOC_κ (Br) and the SOC_λ (C) vectors opposed in **1** when they are approximately parallel⁹ in HCB r ? In a general carbene, both *A* and *B* have a large amplitude at C_λ , one in a $2p_x$ and the other in a $2p_y$ AO (Figure 2), producing a large atomic contribution (SOC_λ) $_z$ along the direction of the vector product $x \times y$.⁶ This contribution can be along z or $-z$, depending on the relative phase of *A* and *B* on C_λ , which determines the sense of rotation around an axis passing through C_λ that is needed to achieve positive overlap of the amplitudes of *A* and *B* on this atom. The vectorial contributions of other atoms are dictated by the amplitudes with which their orbitals enter into *A* and *B*. In a saturated chain, these drop rapidly with distance from the divalent carbon, but if κ is a heavy atom, it can compensate for this falloff by its large Z value. In **1** the amplitude of *B* on Br (4sp NHO) is 20–30% of that on C_λ , and the amplitude of *A* on Br is only about 1% of its amplitude on C_λ . Yet, $|SOC_\kappa|$ (Br) and $|SOC_\lambda|$ (C) are similar.

If the difference in the number of nodes in *A* and *B* located between atoms C_λ and κ is odd, the relative phases of *A* and *B* on atom κ will be the opposite of what they are on C_λ , their two atomic contributions will be opposed, and atom κ will have an inverse

heavy-atom effect. This situation appears to be rare. Figure 2 shows that its origin in the syn conformation of **1** is unusual (the situation in the anti form is similar). For NHO amplitudes at atoms along the CBr chain, one observes the alternation of signs expected for the least stable bonding orbitals in both *A* and *B*, and the relative phases of the two at each atom remain the same. The relative signs of the π -symmetry (lone pair) 4p Br NHO in *A* and of the σ -symmetry (C–Br antibond) 4sp Br NHO in *B* agree with those of the corresponding 2p NHOs on the divalent carbon, and the vector contribution from this orbital pair on Br is indeed parallel to that from C_λ . The nodal pattern in *A* is caused by the lone-pair Br orbital entering in an antibonding fashion relative to the π -symmetry orbital of the neighbor CH_2 group. The dominant contribution by the Br atom originates in the contribution of another of its NHOs to *A*. This is the π -symmetry 4d (Rydberg) NHO, which is high in energy and therefore enters *A* in a bonding fashion relative to the π -symmetry orbital of the neighbor CH_2 group. This reduces the number of nodes by one and reverses the sense of the contribution of the 4d(Br),4sp(Br) orbital pair to SOC_κ .

In the orthogonal conformation ($\omega = 90^\circ$) *A* delocalizes into the C–Br antibond and carries contributions from bromine 4sp (amplitude $\sim 30\%$ relative to C_λ), $4p_z$ (20%), and Rydberg 5d (5%) NHOs. *B* contains Br orbitals with small amplitudes (0.5–2%). In this conformation, too, $(SOC_\kappa)_z$ is negative and is due to the 4sp(Br),5p(Br) and 4d(Br),4sp(Br) orbital pairs, where the Rydberg 4d(Br) and 5p(Br) orbitals again enter with one fewer node.

The SOC value represents an exquisitely sensitive probe of electronic structure. We are not aware of other examples of a significant difference in molecular properties of a low-energy state as a result of involvement by a bromine 4d orbital, or for that matter, a similar orbital on any of the halogens.¹⁰ Of course, few if any other customarily studied molecular properties exhibit such selectively enhanced sensitivity to minute details of molecular electronic structure at a substituent atom. It will be difficult to predict heavy-atom effects on SOC in organic molecules reliably from qualitative considerations of the nature of wave functions based on the customary *I* and *E* electronic effects of substituents. Although inverse heavy-atom effects will probably be quite rare, it appears useful to be aware of their existence in view of their obvious implications for rates of intersystem crossing.

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