

# A DFT study of the hyperfine coupling constants of triplet carbenes and biradicals

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## Abstract

Motivated by our recent investigation of spin–orbit mixing in the simplest singlet carbene, HCF, we report Density Functional Theory (DFT) calculations of the isotropic and anisotropic hyperfine coupling constants (HFCCs) of HCF ( $\tilde{a}^3A''$ ) and other important triplet carbenes and biradicals. We conducted extensive DFT calculations on the prototypical triplet carbene, CH<sub>2</sub>, and compare our results with experimental constants determined from Electron Spin Resonance (ESR) and microwave spectroscopy. We subsequently report DFT calculations of the HFCCs of other prototypical triplet carbenes and biradicals including HCF, HCCN, and C<sub>3</sub>H<sub>2</sub>, and the arylcarbenes diphenylmethylene (DPM; C<sub>13</sub>H<sub>10</sub>) and fluorenylidene (C<sub>13</sub>H<sub>8</sub>). The calculated HFCCs are compared in each case with experimental ESR and microwave data. This study provides an example of the utility of DFT for the calculation of HFCCs of open-shell species.

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**Keywords:** Spin–orbit; Triplet carbenes; Biradicals

## 1. Introduction

Carbenes play an important role in many areas of chemistry [1–5], and simple carbenes have been the target of numerous experimental and theoretical investigations [6–102]. As the smallest carbene with a singlet ground state, HCF is a prototype for understanding the electronic spectroscopy and structure of singlet carbenes [12–32]. In recent articles, we have examined the Renner–Teller (RT) effect and spin–orbit mixing in the HCF  $\tilde{A}^1A'' \leftarrow \tilde{X}^1A'$  system [25–30]. Most recently, we reported a detailed analysis of perturbations in the  $K_a=1 \leftarrow 0$  sub-band of  $2_0^4$ , where both RT and spin–orbit interactions are operative [29]. Our analysis, in combination with Density Functional Theory (DFT) calculations, provided the first glimpse into the properties of the triplet state and the magnitude of the spin–orbit matrix elements [29]. We report here the full results of those calculations.

The literature concerning theoretical studies of the hyperfine coupling constants (HFCCs) of open-shell species

has grown rapidly in the past decade [31–34,103–122], and several excellent reviews are available [112–117]. It is now well documented that isotropic HFCCs are very sensitive to method and basis set, and highly correlated methods in combination with large, well-balanced basis sets are typically needed to reproduce experimental constants [33, 103–106]. Anisotropic HFCCs are less sensitive to factors such as geometry, method and basis set than are isotropic HFCCs, as the latter are determined only at a single point—the nucleus in question. Due to its favorable scaling, density functional theory (DFT) has been increasingly applied to calculate HFCCs of open-shell species [110,116,118–122].

In light of the recent advances in this area, we were surprised to find in the literature few calculations of the HFCCs of triplet carbenes and biradicals. Even for the prototypical triplet carbene, methylene (CH<sub>2</sub>), which has received extensive attention from theorists, only a handful of studies have reported HFCCs [31–34,43,44], and these have typically focused on the isotropic <sup>13</sup>C and <sup>1</sup>H constants. To our knowledge there are no reported DFT studies of the methylene HFCCs. Thus, we first conducted a DFT study of isotropic and anisotropic HFCCs for the  $\tilde{X}^3B_1$  state of methylene, and then, using the developed protocol, calculated HFCCs for other prominent triplet carbenes and biradicals including HCF, HCCN, C<sub>3</sub>H<sub>2</sub>,

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and the arylcarbenes diphenylmethylene (DPM, C<sub>13</sub>H<sub>10</sub>) and fluorenylidene. The results of those calculations and comparisons with experimental data form the basis of this report.

## 2. Computational details

Calculations were performed using the GAUSSIAN 98 or 03 packages on a personal computer [123]. Single point spin unrestricted DFT calculations of the HFCCs were performed on optimized or experimental structures using a variety of functionals (B3LYP [124], BLYP [125,126], PBE0 and PBE1 [127,128], VSXC [129], HCTH [130], B971 [130], B3PW91 [131] and MPWPW91 [132]) in combination with basis sets optimized for the calculation of spectroscopic properties, which included Barone's EPR-II and -III [116], the core-valence correlated cc-pCVTZ and cc-pwCVTZ basis sets of Dunning and co-workers [133,134], and IGLO-II and -III [135].

## 3. Results and discussion

### 3.1. CH<sub>2</sub>

The HFCCs for CH<sub>2</sub> ( $\tilde{X}^3B_1$ ) were first calculated by Morikawa et al. [32] using a SCF MO theory, which yielded an isotropic <sup>13</sup>C constant of 356 MHz, significantly larger than experimental values of 239–249 MHz [35–38]. In contrast, their isotropic <sup>1</sup>H constant of –12 MHz is consistent with subsequent experimental studies which place the value between –12.48(90) and –20.26(51) MHz [39–42]. In 1984, Feller and Davidson [33] reported single and double excitation configuration interaction (SD-CI) calculations which yielded isotropic constants of 236 and –22 MHz. Knight et al. [43] reported values of 239 and –20.5 MHz from multi-reference CISD calculations. Subsequently, Nakatsuji et al. [34] reported symmetry adapted cluster-configuration interaction (SAC-CI) calculations using Gaussian basis sets; the SAC-CI values using a [4s2p1d/2s1p] basis set were 233 and –24.6 MHz. Most recently, Bartlett and co-workers [44] reported a coupled cluster study of the methylene isotropic HFCCs using a variety of basis sets; CCSD(T)/TZ2P calculations on the MBPT(2)/DZP optimized geometry gave values of 247.6 and –18.4 MHz.

We ran a series of DFT calculations on CH<sub>2</sub>( $\tilde{X}^3B_1$ ) using the experimental geometry [ $R_{CH}=1.0766$  Å,  $\theta_{HCH}=134.037^\circ$ ] [35]. A selection of the calculated isotropic <sup>13</sup>C and <sup>1</sup>H HFCCs are compared in Table 1 with the experimental data [35–42]. For the isotropic <sup>13</sup>C constant, we found the best agreement using B3LYP in combination with the triple-zeta EPR-III and IGLO-III basis sets, and PBE1/EPR-III. These methods also worked well for the <sup>1</sup>H constant; values range from –7.3 (B3LYP/IGLO-III) to

Table 1  
Calculated and experimental isotropic hyperfine constants (in MHz) for CH<sub>2</sub> ( $\tilde{X}^3B_1$ )

Method	Basis set	$a_F$ ( <sup>13</sup> C)	$a_F$ ( <sup>1</sup> H)
B3LYP	EPR-II	240.6	–11.1
	EPR-III	238.3	–11.7
	cc-pCVTZ	228.8	–10.1
	cc-pwCVTZ	224.4	–10.1
	IGLO-II	241.3	–13.4
	IGLO-III	237.0	–7.2
BLYP	EPR-II	232.6	–6.9
	EPR-III	227.0	–6.9
	cc-pCVTZ	220.6	–5.2
	cc-pwCVTZ	215.9	–5.3
	IGLO-II	231.5	–9.0
	IGLO-III	225.8	–2.1
PBE0	EPR-II	219.8	–16.5
	EPR-III	216.5	–17.0
	cc-pCVTZ	204.7	–15.0
	cc-pwCVTZ	198.7	–15.0
	IGLO-II	219.8	–18.9
	IGLO-III	214.3	–11.9
PBE1	EPR-II	234.0	–22.3
	EPR-III	232.7	–22.6
	cc-pCVTZ	218.2	–20.5
	cc-pwCVTZ	212.7	–20.5
	IGLO-II	234.4	–24.1
	IGLO-III	229.8	–17.1
<i>Experiment</i>			
Ref. [35]		247	
Ref. [36]		245	
Ref. [37]		249	
Ref. [38]		238.7(555)	
Ref. [39]			–20.26(51)
Ref. [40]			–12.48(90)
Ref. [41]			–13.62(86)
Ref. [42]			–16.81(28)

–22.6 (PBE1/EPR-III), spanning the range of experimental values [39–42]. The latter is in better agreement with previous calculations using CI and coupled cluster theory [33,34,43,44]. In the calculations which follow, we concentrate on the use of the B3LYP, PBE0, and PBE1 functionals in combination with EPR-III and IGLO-III basis sets. However, we note that other combinations produced acceptable results, including VXSC/cc-pCVTZ (233.4, –21.6 MHz), and B971 with cc-pCVTZ (243.4, –13.2) and cc-pwCVTZ (241.4, –13.1). A comprehensive list of our DFT results for CH<sub>2</sub> is provided in the supporting information.

In comparing the calculated anisotropic HFCCs with experiment, it is important to note that calculated HFCCs are referenced to a principal axis system ( $x, y, z$ ) in which the dipolar coupling tensor ( $T$ ) is diagonal [116]. In contrast, experimental constants are usually measured in the inertial axis system ( $a, b, c$ ), and the off-diagonal elements are typically not determined. However, for CH<sub>2</sub> the transformation from principal to inertial axis system requires a simple frame rotation in the molecular plane [136]. In Table 2, we compare a selection of calculated results for the methylene

Table 2  
Calculated and experimental anisotropic hyperfine constants (in MHz) for  $\text{CH}_2(\tilde{X}^3B_1)$

	$^{13}\text{C}$ constants			$^1\text{H}$ constants		
	$T_{aa}$	$T_{bb}$	$T_{cc}$	$T_{aa}$	$T_{bb}$	$T_{cc}$
<i>Calculated</i>						
B3LYP/EPR-III	−155.9	59.3	96.5	60.8	−29	−32
B3LYP/IGLO-III	−155.2	59	96.2	61.7	−29.3	−32.6
PBE0/EPR-III	−154.9	59.9	95	59.1	−28.3	−31
PBE1/EPR-III	−152.9	58.3	94.6	59.9	−28.7	−31.2
<i>Experiment</i>						
Ref. [35]	(−)70	34	35			
Ref. [36]	(−)63	34	30			
Ref. [37]	(−)53	31	25			
Ref. [38]	−65(22)	33(22)	− <sup>a</sup>			
Ref. [39]				39.7(17)	−20.2(19)	− <sup>a</sup>
Ref. [40]				42.09(98)	−21.4	− <sup>a</sup>
Ref. [41]				43.68(87)	−21.9(12)	− <sup>a</sup>
Ref. [42]				32.32(21)	−20.70(36)	− <sup>a</sup>

The theoretical results have been transformed to the inertial axis frame.

<sup>a</sup>  $T_{bb} - T_{cc} = 0$  (assumed).

anisotropic HFCCs with experimental data. The calculated results for the  $^1\text{H}$  constants were transformed to the inertial frame by a rotation of  $22.6^\circ$ . Although the anisotropic constants are much less sensitive to method and basis set, they are consistently larger than experimental estimates. Note that the sign of the  $^{13}\text{C}$  constant was not determined experimentally.

All methylene calculations reported in Tables 1 and 2 and the supporting information were performed using unrestricted wave functions, as the spin contaminations were very small (e.g.  $\langle S^2 \rangle = 2.00$  for the B3LYP/EPR-III calculation). Moreover, there are significant literature precedents for the use of spin-unrestricted wavefunctions in DFT calculations of the HFCC's of open-shell species [110,111,116,118–122]. However, the use of spin-restricted open shell wavefunctions was also investigated. Calculations at the ROB3LYP/EPR-III level yielded isotropic constants for  $^{13}\text{C}$  and  $^1\text{H}$  of 198.1 and 34.5 MHz, respectively; particularly noticeable is the large discrepancy (i.e. wrong sign) for the  $^1\text{H}$  isotropic constant. All of the calculations reported here used the spin-unrestricted theory; as we will show, the spin contamination was small in all cases.

### 3.2. HCF

We subsequently computed the  $^{19}\text{F}$  and  $^1\text{H}$  hyperfine constants for the  $\tilde{a}^3A''$  level of HCF at the optimized B3LYP/EPR-III geometry [ $r_{\text{CH}} = 1.089 \text{ \AA}$ ,  $r_{\text{CF}} = 1.313 \text{ \AA}$ ,  $\theta_{\text{HCF}} = 121.8^\circ$ ], which is similar to that determined previously at the RCCSD(T)/cc-pVQZ level [15]. A selection of calculated hyperfine constants are compared in Table 3 with results from a previous SCF MO calculation [32]. The  $\langle S^2 \rangle$  value for the B3LYP/EPR-III calculation was 2.00, indicating a low degree of spin contamination. As found for methylene, the isotropic and anisotropic HFCCs are of similar magnitude. Although experimental data is lacking for

the  $\tilde{a}^3A''$  state, which is predicted to lie some  $5200 \text{ cm}^{-1}$  above  $\tilde{X}^1A'$  [12–15], we have recently examined in detail triplet-perturbed levels in the  $2_0^4$  band of the  $\text{HCF } \tilde{A}^1A'' \leftarrow \tilde{X}^1A'$  system using polarization quantum beat spectroscopy [29], and have demonstrated success in using DFT calculated constants to reproduce experimental hyperfine splittings.

### 3.3. HCCN

The HCCN radical is notorious, as numerous experimental [45–62] and theoretical [62–72] studies over the past decade have sought to determine whether the ground  $\tilde{X}^3\Sigma^-$  state structure is the bent cyanocarbene **1a** or linear biradical **1b**.

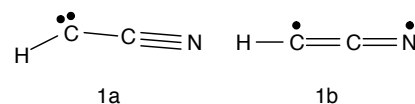


Table 3  
Calculated hyperfine coupling constants for  $\text{HCF}(\tilde{a}^3A'')$

Method/basis set	Nucleus	$a_F$	$T_{xx}$	$T_{yy}$	$T_{zz}$
B3LYP/EPR-III	$^1\text{H}$	96.4	−52.7	−21.7	74.4
	$^{13}\text{C}$	369.9	−153.5	33.2	120.2
	$^{19}\text{F}$	201.8	−517.8	254.1	263.7
B3LYP/IGLO-III	$^1\text{H}$	96.2	−52.3	−22.3	74.5
	$^{13}\text{C}$	370.8	−152.3	31.5	120.8
	$^{19}\text{F}$	202.4	−491.3	243.2	248.2
PBE0/EPR-III	$^1\text{H}$	88.2	−51.2	−20.2	71.4
	$^{13}\text{C}$	342.5	−148	33.2	114.8
	$^{19}\text{F}$	155	−522	260.8	261.2
PBE1/EPR-III	$^1\text{H}$	81	−52.3	−20.6	72.9
	$^{13}\text{C}$	365.9	−150.7	33.4	117.3
	$^{19}\text{F}$	201.2	−501.1	249.1	252
SCF-MO (Ref. [32])	$^1\text{H}$	60	−23	37	14
	$^{13}\text{C}$	475	−60	4	56
	$^{19}\text{F}$	84	−141	92	50

Initial experimental studies in low-temperature matrices using ESR, IR and UV spectroscopy concluded that the ground state was linear [45–48,51], and Dendramis and Leroi [51] suggested for the ground state the allenic structure **1b**. A linear structure was also supported by the mm-wave study of Hirota and co-workers [52]. In 1990, Brown et al. [53] suggested that HCCN was quasi-linear, based upon the unusually short C–H bond length derived for their linear structure. Subsequently, Endo and Ohshima determined the  $^1\text{H}$  and  $^{14}\text{N}$  HFCCs [54], and by comparing the derived constants with related molecules, argued that the allenic structure **1b** was twice as important as **1a**.

Recent experimental studies of vibrationally excited states have provided further support for a quasi-linear structure [55–60]. In a series of high resolution infrared studies [55,57–59], Curl and co-workers measured the  $nv_5^{\pm n}$  vibrational energies of HCCN and DCCN and used semi-rigid bender calculations to estimate the barrier to linearity, which was set at  $256\text{ cm}^{-1}$  for HCCN and  $229\text{ cm}^{-1}$  for DCCN. McCarthy et al. [56] observed rotational transitions from several  $nv_5^{\pm n}$  states and the CCN bending state  $v_4^{\pm 1}$  in addition to three  $l=0$  states, and found that the rotational spectrum was not adequately described by an asymmetric top Hamiltonian. A linear Hamiltonian provided a better description; however, intensity measurements showed that the CCH bending states were lower in energy than expected for a well-behaved linear molecule. A barrier to linearity of  $\sim 235\text{ cm}^{-1}$  was derived.

On the theoretical side, virtually all reports since the late 1970s suggest that the bent cyanocarbene **1a** is the lowest energy structure, in seeming contradiction with the first experimental studies. However, the energy gap between bent and linear forms has narrowed as the level of calculation has increased. In the most recent [CCSD(T)] calculations from Schaefer's group [70], the linear structure **1b** was predicted to lie only  $\sim 277\text{ cm}^{-1}$  higher. This value is consistent with their previous studies [64–66,68], as well as those of Malmquist et al. [67], Aoki et al. [69], and Koput [72]. Other theoretical studies have focused on the thermochemical properties of HCCN [62,71]; however, to our knowledge there have been no calculations of the HFCCs for this radical.

Given the expected quasi-linearity of HCCN, vibrational averaging effects must be considered, and we, therefore, conducted single-point DFT calculations of the HFCCs at HCC bond angles in the range from  $130$  to  $180^\circ$ , using the CCSD(T)/cc-pV5Z optimized geometries at each bond angle [72]. The isotropic constants calculated for  $^1\text{H}$ ,  $^{13}\text{C}_1$ ,  $^{13}\text{C}_2$ , and  $^{14}\text{N}$  using B3LYP, PBE0, and PBE1 with the EPR-II basis set are plotted in Fig. 1 as a function of bond angle, with the experimental  $^1\text{H}$  and  $^{14}\text{N}$  constants of Endo and Ohshima shown as dashed lines in the respective panels. The  $\langle S^2 \rangle$  value for the B3LYP/EPR-III calculation was 2.001, indicating a low degree of spin contamination. From Fig. 1, we see that the isotropic  $^1\text{H}$  and  $^{13}\text{C}_1$  constants are very sensitive to bond angle, changing by factors of

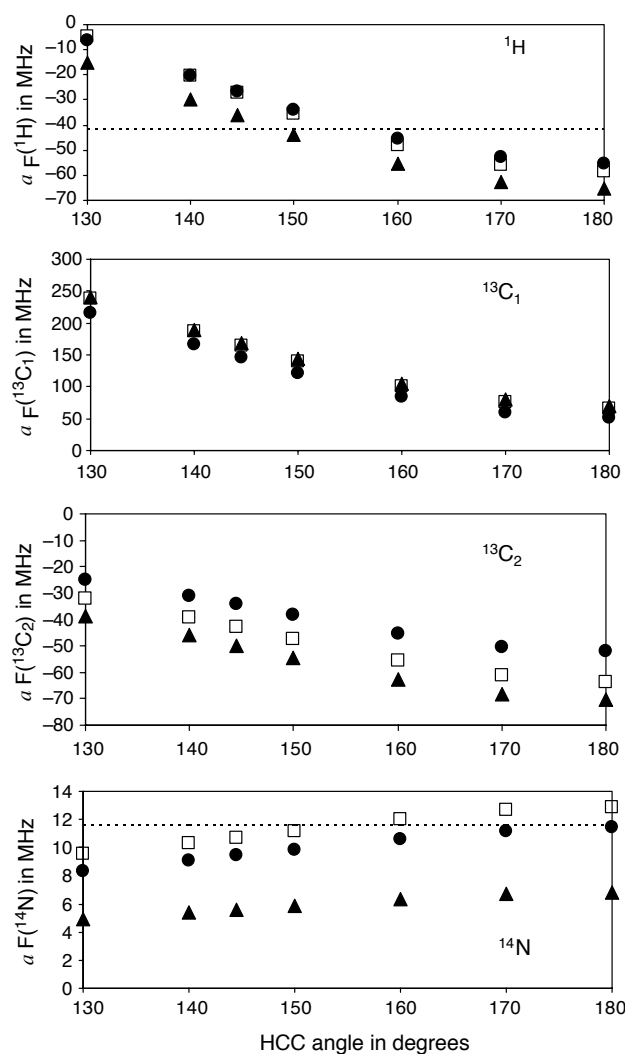


Fig. 1. Calculated isotropic hyperfine coupling constants for HCCN. Legend: ( $\square$ ) B3LYP/EPR-III, ( $\bullet$ ) PBE1/EPR-III, ( $\blacktriangle$ ) PBE0/EPR-III. The experimental results of Endo and Ohshima for  $^1\text{H}$  and  $^{14}\text{N}$  are shown as the dashed lines in the respective panels.

$\sim 10$  and  $\sim 4$ , respectively, across this range. In contrast, the isotropic  $^{13}\text{C}_2$  and  $^{14}\text{N}$  constants change by factors of  $\sim 2$  and  $\sim 1.2$ , respectively. These calculations show that the HFCCs are a sensitive probe of the molecular structure.

Fig. 2 shows the one-dimensional bending potential calculated by Koput [72] at two levels of theory: (a) CCSD(T)/cc-pV5Z, and (b) CASPT2/cc-pV5Z. A semi-rigid bender analysis using the two potentials yielded vibrational energy levels which bracketed the experimentally observed values, and a linear interpolation was used to estimate the barrier height ( $265\text{ cm}^{-1}$ ) and equilibrium HCC angle ( $146.3^\circ$ ) [72]. In Fig. 2, we show the calculated position of the lowest energy level for each potential. It is clear that a large amplitude bending motion is expected, with the effective HCC angle larger than the equilibrium angle by at least several degrees, depending on the potential. Consistent with this expectation, we find (Fig. 1) that

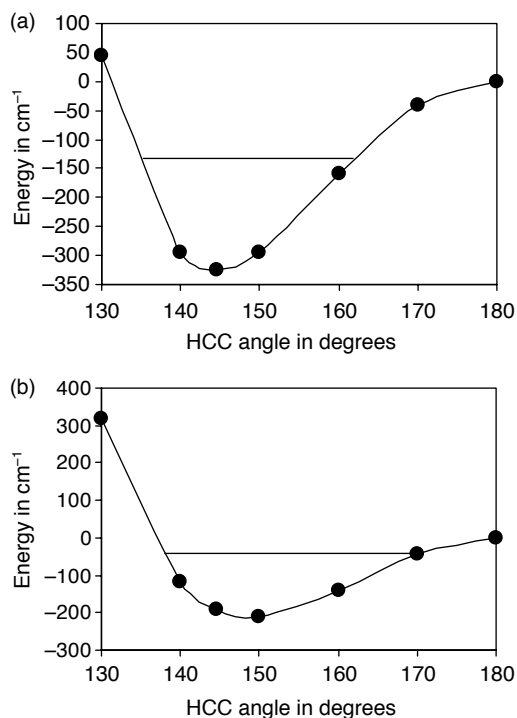


Fig. 2. Calculated one-dimensional bending potentials for HCCN, based on the data reported in Ref. [72]. The PESs were calculated at two levels of theory: (a) CCSD(T)/cc-pV5Z, and (b) CASPT2/cc-pV5Z. The horizontal line in each plot shows the calculated position of the lowest energy level from a semi-rigid bender model.

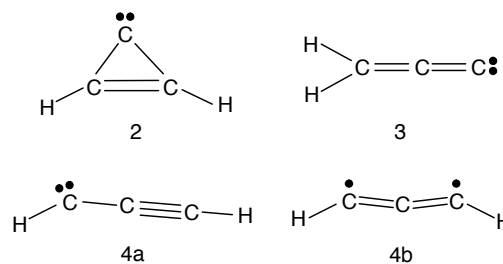
the calculated B3LYP/EPR-III isotropic  $^1\text{H}$  and  $^{14}\text{N}$  constants match the experimental results at an angle of  $\sim 154^\circ$ , or  $\sim 8^\circ$  larger than the estimated equilibrium angle [72]. Thus, the calculated isotropic  $^1\text{H}$  and  $^{14}\text{N}$  constants agree well with experiment and support a bent equilibrium HCCN structure with large amplitude HCC bending motion. Given ambiguities regarding choice of potential and the applicability of the semi-rigid bender model, we have not at this stage attempted a more comprehensive treatment of the effects of vibrational averaging.

The dependence of the calculated (B3LYP/EPR-II) anisotropic constants ( $T_{aa}$ ,  $T_{bb}$ ,  $T_{cc}$ ) on bond angle for the  $^1\text{H}$ ,  $^{13}\text{C}_1$ ,  $^{13}\text{C}_2$ , and  $^{14}\text{N}$  nuclei is shown in Fig. 3. In all cases, a very weak dependence is observed. Comparing with experiment, we note that Endo and Ohshima determined the Frosch and Foley constant  $c$ , which can be taken as  $3/2T_{aa}$ . Their experimental constants (multiplied by  $2/3$ ) for  $^1\text{H}$  and  $^{14}\text{N}$  are shown as dashed lines in the respective panels in Fig. 3. In both cases the experimental result is overestimated by theory.

### 3.4. Triplet $\text{C}_3\text{H}_2$

The  $\text{C}_3\text{H}_2$  radical is an important species in combustion and interstellar chemistry, and the singlet and triplet  $\text{C}_3\text{H}_2$  isomers have been the focus of numerous theoretical studies [73–91]. Experimental studies include gas-phase rotational [92–97], infrared [98], mass and photoelectron

spectra [99], and matrix ESR [46,47], infrared [79,86,100–102], and electronic [85,86,90] spectra. Most of these



have focused on cyclopropenylidene **2**, which is the global minimum on the  $\text{C}_3\text{H}_2$  PES, and propadienylidene (or vinylidencarbene) **3**. There are fewer studies of the triplet propynylidene (or propargylene) **4**, which by analogy with

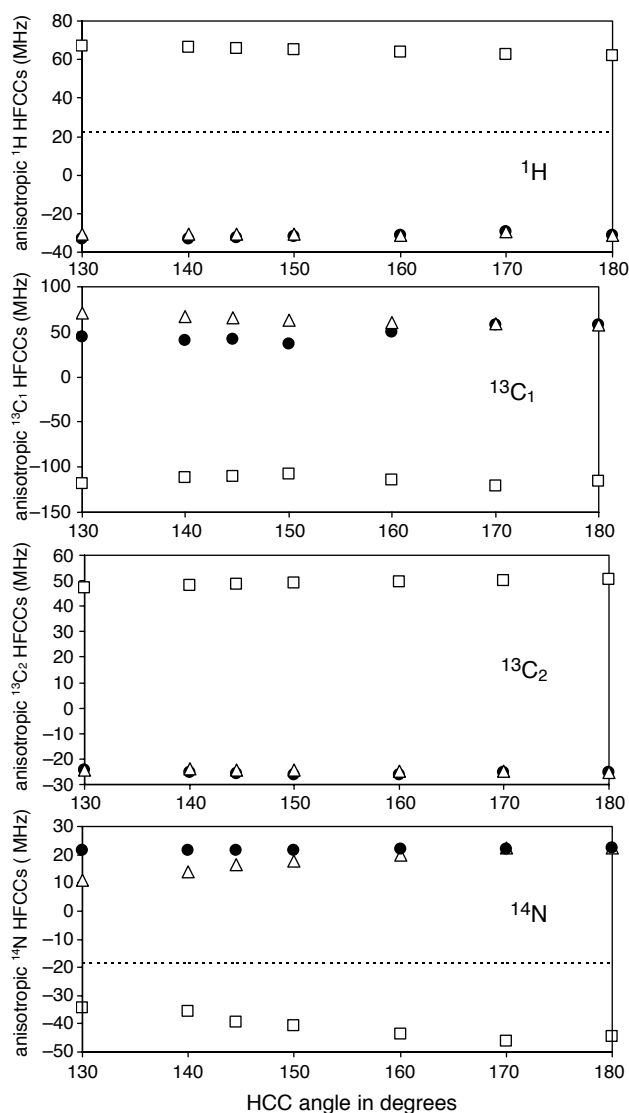


Fig. 3. Calculated anisotropic hyperfine coupling constants for HCCN at the B3LYP/EPR-III level. Legend: ( $\square$ )  $T_{aa}$ , ( $\bullet$ )  $T_{bb}$ , ( $\Delta$ )  $T_{cc}$ . The experimental results of Endo and Ohshima for the  $T_{aa}$  constants of  $^1\text{H}$  and  $^{14}\text{N}$  are shown as the dashed lines in the respective panels.

HCCN can adopt the bent carbene structure **4a** or biradical structure **4b**.

In early work of Benheim et al. [46,47] ESR spectra of (matrix isolated) propynylidene showed a small zero-field splitting parameter which was taken to indicate a linear structure. An early theoretical study predicted a non-planar  $C_2$  structure (**4b**) [73], yet subsequent treatments using perturbation theory indicated a planar  $C_s$  structure (**4a**) [76–78,82,83]. In 1995, McMahon and co-workers [102] used  $^{13}\text{C}$  labeling and matrix infrared and ESR spectroscopy to argue convincingly for the  $C_2$  structure, and recent calculations using CASSCF and coupled cluster methods support this conclusion [84–87]. Calculations at the CCSD(T)/TZP level also find three saddle points corresponding to triplet  $C_s$ ,  $C_{2v}$ , and  $D_{\infty h}$  structures within 3 kJ mol $^{-1}$  of the global minimum [87].

We calculated the hyperfine constants of **4b** using the optimized geometries reported at the CCSD(T)/TZP level [87] and these are listed in Table 4. The  $\langle S^2 \rangle$  value for the B3LYP/EPR-III calculation was 2.002, indicating again a low degree of spin contamination. To date the only experimental information comes for ESR spectra [86,102], where the measured isotropic  $^{13}\text{C}$  hyperfine constants for [1- $^{13}\text{C}$ ] and [2- $^{13}\text{C}$ ] propynylidene were 81 and (–)53 MHz, respectively. These are in good agreement with the B3LYP/IGLO-III values of 79.8 (average of  $C_1$  and  $C_3$ ) and –46.2 MHz. Although triplet propynylidene is predicted to have a significantly smaller dipole moment than the singlet isomers **2** and **3** [84], it should be detectable by microwave spectroscopy, and we hope that a gas-phase

Table 4

Calculated hyperfine coupling constants (in MHz) for triplet propynylidene ( $\text{C}_3\text{H}_2$ ), using the optimized geometry from Ref. [87]

Method/Basis Set	Nucleus	$a_F$	$T_{xx}$	$T_{yy}$	$T_{zz}$
B3LYP/EPR-III	$^1\text{H}_1$	–33.9	–25.1	–24.2	49.3
	$^{13}\text{C}_1$	93.0	54.4	48.9	–103.3
	$^{13}\text{C}_2$	–49.0	–24.4	–24.2	48.5
	$^{13}\text{C}_3$	87.5	55.3	49.3	–104.5
	$^1\text{H}_2$	–36.6	–25.1	–24.6	49.7
	B3LYP/IGLO-III	$^1\text{H}_1$	–33.5	–26.3	–25.4
$^{13}\text{C}_1$		82.6	55.7	50.1	–105.8
$^{13}\text{C}_2$		–46.2	–24.9	–24.6	49.5
$^{13}\text{C}_3$		78.0	56.7	50.4	–107.1
$^1\text{H}_2$		–36.0	–26.4	–25.8	52.3
PBE0/EPR-III		$^1\text{H}_1$	–31.3	–23.7	–22.7
	$^{13}\text{C}_1$	77.3	51.7	47.0	–98.6
	$^{13}\text{C}_2$	–40.6	–20.4	–20.2	40.6
	$^{13}\text{C}_3$	71.6	52.5	47.5	–100.0
	$^1\text{H}_2$	–33.8	–23.7	–23.1	46.8
	PBE1/EPR-III	$^1\text{H}_1$	–40.8	–25.2	–24.3
$^{13}\text{C}_1$		96.9	55.0	49.5	–104.5
$^{13}\text{C}_2$		–57.6	–27.1	–27.0	54.2
$^{13}\text{C}_3$		91.8	55.9	50.0	–105.9
$^1\text{H}_2$		–43.6	–25.2	–24.6	49.9

study of the hyperfine structure of this important biradical will be forthcoming.

### 3.5. Triplet DPM and fluorenylidene

Finally, we examined the triplet arylcarbenes diphenylmethylene (DPM) and fluorenylidene. The arylcarbenes are an important class of carbenes, whose structure, spectroscopy, and reactivity have received extensive scrutiny in the literature [1,2]. Early EPR studies established DPM as a triplet and investigated the hyperfine structure associated with  $^{13}\text{C}$  substitution at the central carbon [1,2,137–139]. The first ENDOR study of arylcarbenes was carried out on fluorenylidene [140,141], and subsequent ENDOR studies of DPM in 1,1-diphenylethylene and benzophenone single crystals resolved the proton hyperfine structure [142], which was compared with results from INDO calculations.

Table 5

Calculated hyperfine coupling constants (in MHz) for triplet diphenylmethylene ( $\text{C}_{13}\text{H}_{10}$ )

Method/basis set	Nucleus	$a_F$	$T_{xx}$	$T_{yy}$	$T_{zz}$
B3LYP/EPR-III	$^{13}\text{C}_1$ <sup>a</sup>	160.6	36.8	85.0	–121.9
	$^1\text{H}_3$	–7.8	–6.5	–1.8	8.3
	$^1\text{H}_4$	3.7	–2.9	–0.8	3.7
	$^1\text{H}_5$	–8.0	–9.5	–0.2	9.7
	$^1\text{H}_6$	6.0	–3.0	–0.5	3.5
	$^1\text{H}_7$	–8.3	–5.7	–3.3	9.0
	B3LYP/IGLO-III	$^{13}\text{C}_1$	161.0	37.6	84.4
$^1\text{H}_3$		–7.1	–6.8	–1.7	8.5
$^1\text{H}_4$		3.3	–2.8	–0.9	3.7
$^1\text{H}_5$		–7.2	–9.5	–0.5	10.0
$^1\text{H}_6$		5.5	–3.0	–0.6	3.7
$^1\text{H}_7$		–7.6	–6.0	–3.4	9.4
PBE0/EPR-III		$^{13}\text{C}_1$	142.2	31.7	83.6
	$^1\text{H}_3$	–6.4	–6.4	–1.5	7.9
	$^1\text{H}_4$	2.5	–2.7	–0.1	2.8
	$^1\text{H}_5$	–6.8	–8.5	–0.2	8.7
	$^1\text{H}_6$	5.0	–2.9	0.1	2.8
	$^1\text{H}_7$	–6.8	–5.7	–2.5	8.2
	PBE1/EPR-III	$^{13}\text{C}_1$	165.4	39.2	83.1
$^1\text{H}_3$		–9.1	–6.2	–2.0	8.3
$^1\text{H}_4$		4.7	–3.0	–1.4	4.4
$^1\text{H}_5$		–9.2	–10.1	0.1	10.0
$^1\text{H}_6$		6.9	–3.2	–1.2	4.4
$^1\text{H}_7$		–9.5	–5.5	–3.8	9.3
Experiment		$^{13}\text{C}_1$ <sup>b</sup>	144.9	21.6	32.3
	$^{13}\text{C}_1$ <sup>c</sup>	173.3	16.3	41.5	–57.8
	$^1\text{H}_3$	–7.37	–0.26	0.86	–0.60
	$^1\text{H}_4$	2.92	–0.84	–0.41	1.25
	$^1\text{H}_5$	–7.74	–1.68	–2.25	3.93
	$^1\text{H}_6$	4.51	–0.99	–0.33	1.32
	$^1\text{H}_7$	–7.75	–0.19	1.21	–1.03

<sup>a</sup>  $\text{C}_1$  is the divalent carbon.

<sup>b</sup> For DPM trapped in 1,1'-diphenylethylene single crystals.

<sup>c</sup> For DPM trapped in dibenzophenone single crystals.

Table 6  
Calculated hyperfine coupling constants (in MHz) for triplet fluorenylidene ( $C_{13}H_8$ )

Method/basis set	Nucleus	$a_F$	$T_{xx}$	$T_{yy}$	$T_{zz}$
B3LYP/EPR-III	$^{13}C_1^a$	241.0	30.9	89.0	−119.9
	$^1H_3$	−5.8	−4.4	−2.5	6.9
	$^1H_4$	6.8	−3.1	−0.1	3.2
	$^1H_5$	−6.6	−7.7	−0.6	8.3
	$^1H_6$	2.5	−2.4	−0.6	3.0
	B3LYP/IGLO-III	$^{13}C_1$	241.1	31.1	88.7
$^1H_3$		−5.5	−4.6	−2.3	6.9
$^1H_4$		5.8	−3.0	0.1	3.0
$^1H_5$		−4.7	−7.5	−0.9	8.3
$^1H_6$		1.7	−2.4	−0.6	2.9
PBE0/EPR-III		$^{13}C_1$	219.6	25.0	88.8
	$^1H_3$	−3.7	−4.3	−2.0	6.3
	$^1H_4$	5.9	−3.0	0.2	2.8
	$^1H_5$	−5.1	−6.6	−0.7	7.3
	$^1H_6$	0.8	−2.3	−0.5	2.8
	PBE1/EPR-III	$^{13}C_1$	245.8	34.1	85.3
$^1H_3$		−6.7	−4.2	−2.7	6.9
$^1H_4$		7.0	−3.1	−0.4	3.6
$^1H_5$		−7.4	−8.1	−0.4	8.5
$^1H_6$		3.1	−2.5	−0.9	3.4
Experiment		$^{13}C_1$	263.6	16.4	43.8
	$^1H_3$	−4.44	−2.09	−0.35	1.75
	$^1H_4$	5.41	−1.42	1.15	0.28
	$^1H_5$	−5.54	−0.19	0.11	0.08
	$^1H_6$	1.21	−0.98	0.19	0.79

<sup>a</sup>  $C_1$  is the divalent carbon.

We optimized the structure of DPM at the B3LYP/6-31G(p,d) level, and subsequently performed single point DFT calculations to determine the  $^{13}C$  and  $^1H$  HFCCs. The optimized structure featured a dihedral angle of  $29.1^\circ$ , compared with the experimental value of  $34^\circ$  for DPM isolated in 1,1'-diphenylethylene single crystals [142]. Note that the latter may not represent the equilibrium geometry of the free molecule due to distortions imposed by the matrix. The calculated HFCCs are compared in Table 5 with experimental data from EPR and ENDOR measurements, where we used the atom labeling scheme of Ref. [142]. The agreement is excellent for the isotropic constants, particularly when using the B3LYP functional with EPR-III or IGLO-III; again the anisotropic constants are overestimated. Note that the DFT calculations quantitatively reproduce the observed oscillation in the proton isotropic HFCCs in going around the phenyl ring.

The structure of fluorenylidene was optimized at the B3LYP/6-31G(p,d) level, with subsequent single point DFT calculation of the  $^{13}C$  and  $^1H$  HFCCs performed. The optimized structure was planar, with  $\angle CCC = 111.9^\circ$  about the divalent carbon. The calculated HFCCs are compared in Table 6 with experimental data from EPR and ENDOR measurements, where the atom labeling scheme of Ref. [141] was used. The agreement is quite good for

the isotropic constants; note that the PBE0 functional best reproduces the experimental isotropic  $^1H$  constants.

The  $\langle S^2 \rangle$  values for the B3LYP/EPR-III calculations were 2.002 and 2.001 for DPM and fluorenylidene, respectively, again indicating a low degree of spin contamination.

#### 4. Summary and conclusions

Inspired by experimental studies of spin-orbit mixing in the simplest singlet carbene, HCF, we conducted a DFT study of the hyperfine coupling constants of a series of triplet carbenes and biradicals. For the prototypical triplet carbene,  $CH_2$ , we have shown that DFT can accurately reproduce isotropic experimental HFCCs from ESR and microwave data, and in particular the B3LYP, PBE0, and PBE1 functionals in combination with specialized basis sets such as the triple zeta sets EPR-III and IGLO-III perform well. We subsequently used DFT to calculate HFCCs for a series of important triplet carbenes and biradicals including HCF, HCCN,  $C_3H_2$ , and the arylcarbenes diphenylmethylene ( $C_{13}H_{10}$ ) and fluorenylidene ( $C_{13}H_8$ ). Where they can be compared, the calculated isotropic constants are in good agreement with experimental data from ESR and microwave measurements. This work has provided another example of the utility of DFT for the calculation of HFCCs of open-shell species.

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#### Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.theochem.2005.03.035](https://doi.org/10.1016/j.theochem.2005.03.035)

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