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Matrix isolation ESR spectroscopy and quantum chemical calculations on 5-methylhexa-1,2,4-triene-1,3-diyl, a highly delocalized triplet "hybrid" carbene†

Eugenii Ya. Misochko,[*a] **Alexander V. Akimov,**[a] **Denis V. Korchagin,**[a] **Artem A. Masitov**[a] **and Konstantin N. Shavrin**[b]
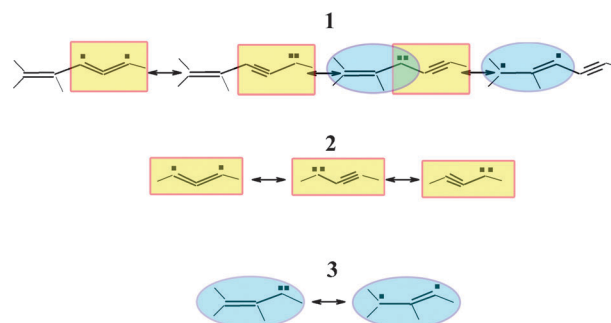
The ESR spectrum of 5-methylhexa-1,2,4-triene-1,3-diyl (**1**) was recorded in an argon matrix at 15 K. The derived zero-field splitting (ZFS) parameters ($D = 0.5054 \pm 0.0006$ cm^{-1} and $E = 0.0045 \pm 0.0002$ cm^{-1}) fall between those determined previously for propargylene (**2**) and vinylcarbene (**3**). DFT and *ab initio* (CAS and MRCI) quantum-chemical calculations of the ZFS parameters of **1**, **2**, and **3** were performed. These calculations indicate that multireference methods are needed to successfully predict ZFS parameters of delocalized carbenes/biradicals such as **1–3**. The calculated singly occupied MOs and spin density distributions show that the spin is more delocalized in **1** than in **2** and **3**, indicating that **1** is a "hybrid" of the constituent ethynyl- and vinylcarbenes, **2** and **3**, respectively. The dominant contribution to the *D*-value in **1** and **2** is found to result from spin–spin interactions on the C atoms of the propylidene moiety, which is strongly affected by spin polarization. Accurate values for the *D*-parameter are also predicted for other types of delocalized triplet carbenes such as HC$_5$H and HCCN.

Introduction

Carbon-chain molecules such as HC$_n$H ($n = $ odd) and H$_2$CC(H)CH have triplet ground states where both unpaired electrons are delocalized. Such open-shell species are important intermediates in reactions of atomic carbon with hydrocarbons,[1] in fuel-rich hydrocarbon flames,[2] as well as in interstellar space.[3] The structure and reactivity of these species has attracted attention and stirred up controversies for decades, for example with regard to their categorization as carbenes or biradicals (see ref. 4–6, and references cited therein). The prevailing current view is that they should be viewed as mixtures of both types of resonance structures (*vide infra*). In 2009, an unusual "hybrid" triplet hydrocarbon composed of a vinyl- and an ethynylcarbene moiety, 5-methylhexa-1,2,4-triene-1,3-diyl (**1**), was detected in an Ar matrix by FTIR spectroscopy.[7] The molecular structure of this "hybrid" carbene/biradical was depicted as the 1,3-biradical:
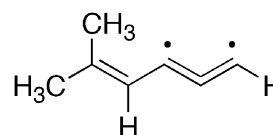
On the other hand, the reported chemical properties of this molecule suggested that other resonance structures, such as those shown in Scheme 1, should also be taken into consideration. Which of these resonance structures participates (or dominates) in the electronic structure of **1** expresses itself in the distribution of the spin density caused by the two unpaired electrons, a property which manifests itself in the ESR spectrum. In particular, the zero-field-splitting (ZFS) parameters *D* and *E*, which can be derived from triplet

[a] *Institute of Problems of Chemical Physics of the Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. E-mail: misochko@icp.ac.ru*
[b] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Leninsky prospekt 47, Russian Federation*
† Electronic supplementary information (ESI) available: (1) Cartesian coordinates of carbenes under consideration; (2) calculated hyperfine interaction constants for carbene **1**; (3) the accuracy of the measurements of the parameters *D* and *E*; (4) calculated parameter *D* of carbenes **1**, **2**, and **3** with various basis sets and reference wave functions. See DOI: 10.1039/c2cp22853j

Scheme 1 Resonance structures of triplet hydrocarbons **1–3**.

ESR spectra, contain information on the distribution of the two unpaired electrons. On the other hand, the spin density distribution can be modelled by quantum chemical calculations, and the accord between experimental and calculated ZFS parameters may be taken as an indication of whether the spin density distribution is modelled correctly. It is the aim of this paper to use such a combined approach to characterize the electronic structure of **1** and similar species.

Background

Spectroscopic parameters derived from ESR spectra (such as hyperfine (hf) interaction tensors and scalar parameters D and E of the ZFS-tensor) give valuable information about the electron spin populations and spatial separation of unpaired electrons. By comparing theoretical and experimental hf parameters, one can check the quality and reliability of quantum chemical calculations and assess spin populations on different atoms. Currently, such an approach is widely used in studies of doublet radicals.[8] Recently this approach was applied in the isotopic (^{13}C) labeling ESR studies of triplet propargylene **2** demonstrating strong spin-polarization on the central carbon atom of the molecule.[6d] However, the hf parameters provide no information on the spatial separation of unpaired electrons in triplet species. This information can be obtained from the ZFS parameter D. A high value of D indicates a close proximity of two spins. For example, unpaired spins in triplet methylene are localized on the same atom, and their strong dipolar coupling gives a large value of $D_{CH_2} = 0.74$–0.78 cm^{-1}.[9] Acetylenic carbenes, like HC_3H and HC_5H, represent more complicated cases. Despite high delocalization of both unpaired electrons, a large magnitude of the ZFS parameter $D = 0.62$–0.64 has been obtained experimentally.[6,10] The semiempirical explanation of this phenomenon was introduced by Wasserman in 1965.[11] A high value of the parameter D was explained by delocalization of both unpaired electrons on odd-numbered carbon atoms, whereas negative electron spin density occupies even-numbered carbon atoms due to strong spin-polarization effects. As a result, one-center spin–spin interactions (the interactions of two spins localized on the same atom) on all carbon atoms provide a dominant contribution to the parameter D, which can be estimated by the following equation:

$$D \cong D_{CH_2} \times \sum_i (\rho_{xi} \times \rho_{yi}), \qquad (1)$$

where ρ_{xi} and ρ_{yi} are electron spin densities of two unpaired electrons on the i-th carbon atom. This equation shows that the parameter D is sensitive to the electron spin density of two unpaired electrons on the same carbon atom. Since 1965, eqn (1) has widely been used in estimations of the parameter D for different carbenes. Attempts to apply multiconfiguration (MCSCF and MRCI) *ab-initio* calculations to vinylmethylene **3** showed strong dependence of σ–π interactions from molecular geometry.[12] Even relatively small errors in the geometry calculations lead to large errors in the parameter D. Various quantum-chemical approaches for calculating the ZFS parameters have appeared recently.[13,14] However, none of these approaches has been applied so far to describe the ZFS parameters of chain triplet carbenes.
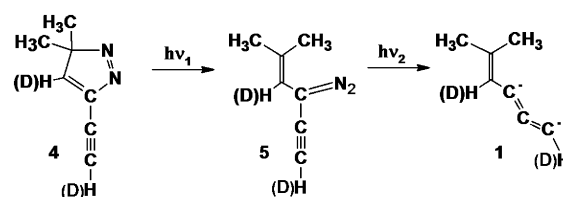
Methods

A. Experimental

3*H*-Pyrazoles **4** (5-ethynyl-3,3-dimethyl-3*H*-pyrazole and 3,3-dimethyl-4-deutero-5-deuteroethynyl-3*H*-pyrazole) as photolytic precursors of **1** were synthesized according to the published methods.[15] Triplet carbene **1** and its deuterated analog **1d** were generated in solid argon matrices by means of the method described in the previous paper.[7]

The experimental technique and apparatus for low-temperature matrix-isolation ESR spectroscopy have been described previously.[16] Solid argon films doped with 3*H*-pyrazole **4** were prepared by vacuum co-deposition of two separate molecular beams (Ar and 3*H*-pyrazole **4** vapor) onto a substrate (sapphire rod) held at 15 K in a high vacuum chamber. Freshly prepared polycrystalline powder **4** was placed in a quartz flask connected to a matrix-isolation apparatus by means of a metering valve. The sublimating polycrystalline powder **4** produced a vapor pressure of $\sim 10^{-4}$ Torr in a flask at room temperature. Deposition of the vapor **4** was carried out through the metering valve simultaneously with argon flow. The rate of 3*H*-pyrazole **4** deposition was estimated in the separate experiments using the interferometric method.[16a] The gas flow rate from the argon channel was adjusted by a needle valve and measured by using a manometer. The gas flow was chosen to obtain the ratio Ar/3*H*-pyrazole **4** $\sim 10^4$. The deposition rate was typically 10 μmol min^{-1}, the thickness of the deposited argon films was typically 100 μm. Temperature stability of the samples was ~ 0.1 K over 15–40 K range. ESR spectra were recorded using a standard 9 GHz spectrometer at low enough microwave power to avoid the saturation effects. Shape and resonance magnetic fields of all components in the ESR spectra did not change in the temperature range of 15–30 K.

Photolysis of the samples was carried out at temperature 15 K by means of the Hg arc lamp (Mercury Spectral Line Lamp, LOT-Oriel) equipped with LOT-Oriel narrow band interference (half bandwidths of *ca.* 10 nm) filters. In order to obtain carbene **1** in high yield, a series of preliminary measurements under varying photolysis conditions were performed. The optimum photolytic procedure consists of subsequent photolysis by two wavelengths. Initially, irradiation of matrix-isolated **4** was performed with light at 365 nm until weak ESR lines of triplet species appeared in the spectra. On further irradiation with light at 297 nm, intensities of ESR lines reached their maxima. If the exhaustive photolysis of the sample was performed only at 365 nm, intensities of ESR lines were three to four times weaker than those observed in the two-stage photolytic procedure. The effective two-stage photolytic formation of triplet species corresponds to a two-stage conversion of precursor (**4**) to (**1**) *via* intermediate (**5**), as it was observed in previous FTIR studies.[7]

B. Computational methods

The equilibrium geometries of carbenes **1**–**3** were optimized with the TZVP basis set[17] using a complete active space self-consistent field (CASSCF) method by the Gaussian-03 program.[18] An 8-electron, 8-orbital active space, hereafter designated (8,8), was used for carbene **1**. The active spaces of carbenes **2** and **3** were designated as (6,6) and (4,4), respectively. Vibrational frequency calculations were carried out at the same level of theory in order to confirm that the optimized structures correspond to the minimum of the potential surface.

Different quantum chemical methods were applied for calculations of the ZFS parameters. The ZFS parameters were calculated by the ORCA program package[19] with two approaches based on McWeeny–Mizuno[13a,20,21] and multi-configurational *ab initio* formalisms.[14] One-electron spin density matrices for evaluation of the spin–spin part of the *D*-tensor in a McWeeny–Mizuno equation have been obtained on the basis of restricted open-shell (RODFT) and unrestricted (UDFT) Kohn–Sham reference determinants,[21] as well as from CASSCF wave functions in a mean-field approximation for comparison.[14a,d] In the second case, *ab initio* values of the *D*-tensor (including both spin–spin and spin–orbit contributions) were obtained employing CASSCF, CASCI and MRCI wave functions with up to 50 triplet and up to 50 singlet roots on top of the State Average (SA)-CASSCF wave function. The reference wave functions were averaged over one triplet (ground state) and one or two (first and second excited states) singlet roots (denoted below as T1, T1S1, and T1S2, respectively) to calculate the spin–orbit contribution by the procedure described in ref. 14a and e. The spin–spin contribution has been evaluated using a two electron spin–spin coupling operator over many-electron wave functions as described earlier.[14]

DFT calculations were carried out with the non-hybrid density functional PBE[22] and a number of basis sets (DZ, DZP, TZV, TZVP, TZVPP, EPRII, EPRIII) which had shown good results in previous test calculations.[21,23,24] All of the *ab initio* calculations of the ZFS parameters were performed with the electronic basis set SVP. Preliminary tested calculations revealed no sufficient influence of the size of the basis set and the reference wave functions on the accuracy of the calculated parameters (see ESI†).

Results and discussion

A. Powder ESR spectrum of carbene 1

Photolysis of matrix-isolated 3*H*-pyrazole **4** leads to the ESR spectrum of a triplet species. In accordance with previous FTIR studies,[7] this triplet species is assigned to carbene **1**. The recorded ESR spectrum (Fig. 1) exhibits four ESR lines, attributable to randomly oriented triplet molecules with a non-zero ZFS parameter *E*.

The Zeeman energy levels and ESR transitions for canonical orientations of the tensor *D* toward external magnetic fields **H**, $\mathbf{H}\|D_X$, $\mathbf{H}\|D_Y$, and $\mathbf{H}\|D_Z$ are displayed in Fig. 2. Two ESR lines at low (215.5 mT) and high (865.6 mT) magnetic fields correspond to parallel components z_1 and z_2, respectively. The most intense doublet ESR line at intermediate magnetic fields
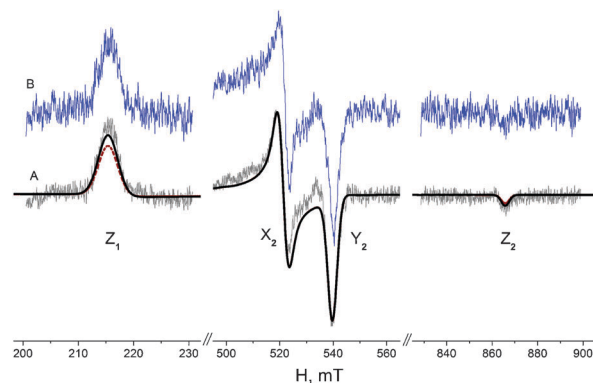

Fig. 1 An ESR spectrum of the photolyzed sample Ar/3*H*-pyrazole **4** $\approx 10^4$ at 15 K (A). An ESR spectrum of the photolyzed sample Ar/deuterated 3*H*-pyrazole **4d** $\approx 10^4$ at 15 K (B). Microwave frequency ν_0 = 9.11245 GHz. Simulated powder spectra of the triplet carbene at 15 K with D = +0.5054 cm^{-1} and E = 0.00445 cm^{-1} shown by solid line, and with D = −0.5054 cm^{-1} and E = 0.00445 cm^{-1} shown by dashed line. Both simulated spectra are normalized to the X_2Y_2 line of the experimental spectrum.
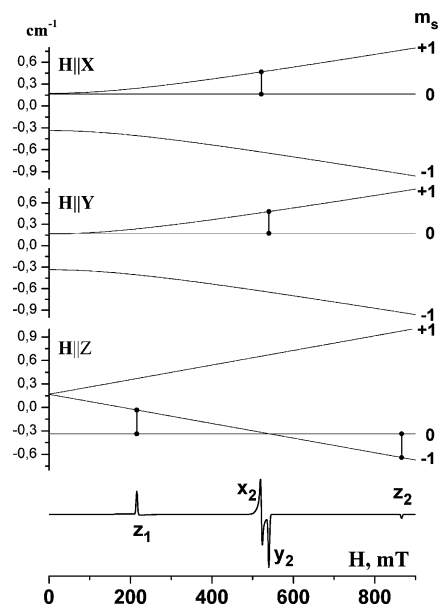

Fig. 2 Calculated Zeeman energy levels, allowed transitions, and a simulated powder ESR spectrum of triplet carbene with D = 0.5054 cm^{-1} and E = 0.0045 cm^{-1}. Simulations were performed using the *EasySpin* program package,[25] operating with an exact numerical matrix diagonalization analysis of the spin Hamiltonian $H = g\beta HS + S\hat{D}S$, S = 1.

is assigned to perpendicular ESR transitions x_2 (521.3 mT) and y_2 (539.6 mT). It should be noted that the recorded spectrum shows no spectrally resolved splitting of different matrix sites, as it was observed in the ESR spectra of matrix-isolated HC$_3$H and HC$_5$H.[6] This allows one to perform a rather simple assignment of ESR lines, and subsequently, to derive unambiguously the ZFS parameters (see below).

Typical line widths in the recorded spectra are equal to *ca.* 3.5 mT. This is somewhat broader than that recorded earlier[6,10] for matrix-isolated carbenes HC$_3$H and HC$_5$H (estimated line width in those spectra equal to *ca.* 1.5–2.5 mT).

We suppose that the line shapes in the spectrum of **1** are determined by an unresolved hyperfine structure on eight protons. Quantum chemical calculations predict that isotropic hf constants on two hydrogen atoms $A_{iso} \approx 1.7$ mT and on protons of two CH$_3$ groups $A_{iso} \approx 0.8$ mT (see ESI†). To check the influence of large hf splittings on the line broadening as well as to verify the influence of vibrational and librational dynamics on the ZFS parameters, we have generated carbene **1d** by the photolysis of deuterated 3*H*-pyrazole **4d**. The ESR spectra in Fig. 1 demonstrate that isotopic H → D substitution of two hydrogen atoms results in an identical spectrum, and subsequently, identical ZFS parameters. Seemingly, the shape of ESR lines is determined mainly by unresolved hyperfine structure on six protons of two CH$_3$ groups.

B.   ZFS parameters of carbene 1

The ZFS parameters D and E yielding the best approximation to the true values were evaluated by minimization of the functional R, which was defined as a root-mean-square (rms) deviation of calculated resonance fields, $H_k(\text{calc})$, from those measured experimentally, $H_k(\text{exp})$:

$$R = \sqrt{\frac{1}{n}\sum_{k=1}^{n}\left(H_k(\text{calc}) - H_k(\text{exp})\right)^2}$$

where $n = 3$ denotes the number of selected lines in the spectrum, z_1, x_2, and y_2.

The resolution of the experimental ESR spectrum allows measuring resonance fields with accuracy of ±0.5 mT. We did not use z_2-line in the calculations due to its very low intensity. The optimized spectrum (Fig. 1) was obtained at $D = 0.5054$ cm^{-1} and $E = 0.0045$ cm^{-1}. It corresponds to the rms deviation of $R(\text{min}) = 0.02$ mT, *i.e.* a practically ideal agreement between experimental and calculated resonance fields was achieved. To estimate an accuracy of the D and E measurements, the rms deviations were calculated by varying each of the parameters close to their optimum values. The rms deviation of $R = 3.5$ mT was chosen as a crucial one, if at least one of the tested lines had deviation $|H(\text{calc}) - H(\text{exp})|$ exceeding the line width. This treatment gave the experimental errors for D and E that were not more than ±0.0006 and ±0.0002 m^{-1}, respectively (see ESI†). Comparison of the measured ZFS parameters with those of vinylcarbene **3** and propagylene **2** showed that the parameters D and E of **1** fall between the parameters of **2** and **3**: $D(\mathbf{3}) < D(\mathbf{1}) < D(\mathbf{2})$ and $E(\mathbf{2}) < E(\mathbf{1}) < E(\mathbf{3})$.

We assumed positive sign of D (as it is shown in Fig. 2) that is typical for carbenes. If the sign of D is negative, the Zeeman energy levels are aligned inversely relative to those shown in Fig. 2. It does not affect the position of the lines. But the sign of D influences the relative intensities of the lines at low temperature due to changes in the populations of the energy levels. The simulated model spectra at 15 K for positive and negative signs are shown in Fig. 1. A positive sign of D is supported by a better fit to the experimental spectrum.

C.   Computational results

The geometry parameters calculated for triplet carbenes **1**, **2** and **3** at the CASSCF/TZVP level of theory are shown in Fig. 3.
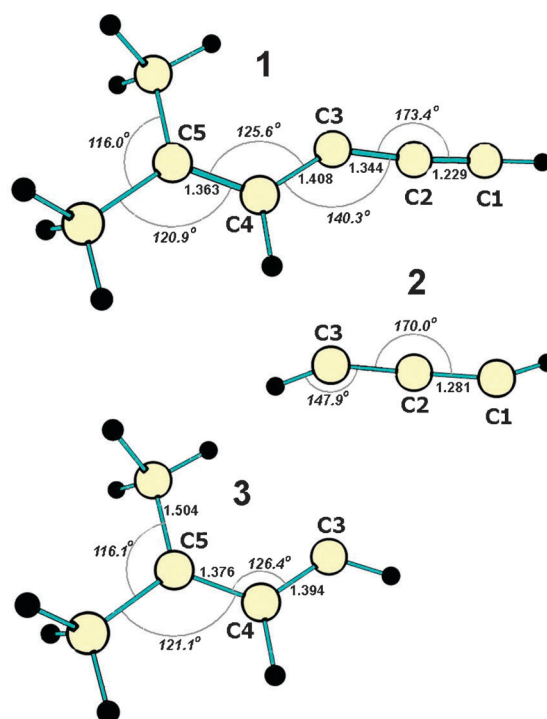

Fig. 3 Computed molecular structures for triplet carbenes **1** (Me$_2$CC(H)CCCH), **2** (HCCCH), and **3** (Me$_2$CC(H)CH); (CASSCF/TZVP).

The structural parameters of **1** are close to those previously calculated at the DFT B3LYP/TZ2P level of theory.[7] The structure of **2** corresponds to a twisted C$_2$ structure, and its structural parameters are close to those recently calculated at the QCISD/6-311 + G(2df,p) level.[6d] However, in our calculations this molecule is a bit more bent. The angle HCC is equal to 148° *vs.* 162° in previous calculations.

The calculated and experimental parameters D of carbenes **1**, **2**, and **3** are shown in Fig. 4. The data are obtained by *ab intio* CASCI(T1S2) calculations, accounting for both spin–spin and spin–orbit contributions. In all cases, a good agreement between theoretical and experimental D values is observed despite very complex electronic structures of the
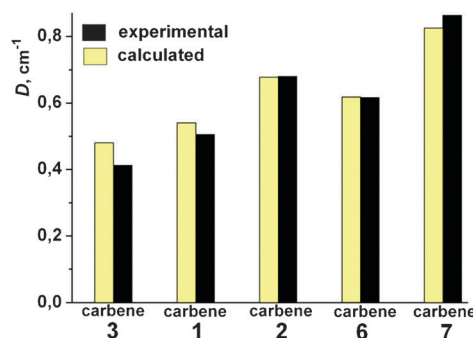

Fig. 4 Calculated parameters D of carbenes **1**, **2**, **3**, **6**, and **7** with comparison to the experimental ones. The data were obtained in *ab intio* CASCI(T1S2) calculations, including both spin–spin and spin–orbit contributions. Experimental data for carbene **2** from ref. 6d, carbene **3** from ref. 26, carbene **6** from ref. 10a, carbene **7** from ref. 27, carbene **1** from this work.

carbenes (see above Scheme 1). Also, the calculations correctly predict the experimental relations $D(3) < D(1) < D(2)$. The CASCI calculations show that contributions of the spin–orbit coupling to the parameter D do not exceed 0.03 cm^{-1}, hence confirming that contributions of the spin–spin interactions to the parameters D are dominant. Below we consider only the spin–spin (SS) interactions.

D. DFT calculations of the ZFS parameters

First, we consider DFT calculations to analyze all factors affecting the ZFS parameters. Recent studies have shown that approaches based on the McWeeny–Mizuno equation gave quite accurate D_{SS} tensors for a series of triplet carbenes and nitrenes, when such approaches were combined with the spin density matrices constructed from DFT calculations.[13g,21,23] However, consensus has not been reached yet how to best calculate the ZFS parameters in a DFT framework (see discussions in ref. 13g, 14c, 21, 23, and 24). There are three fundamental problems in DFT calculations based on the McWeeny–Mizuno equation:[13g,14c,21,23]

1. The RODFT approach cannot express spin polarization effects by definition. This approach gives non-realistic spin density distribution in molecules with strong spin polarization effects and has a tendency to underestimate the calculated D_{SS} values.

2. The unrestricted approach takes into account spin polarization effects and gives more realistic spin distributions. However, the unrestricted wave functions are contaminated by states of higher spin multiplicity which results in over-estimations of D_{SS}.
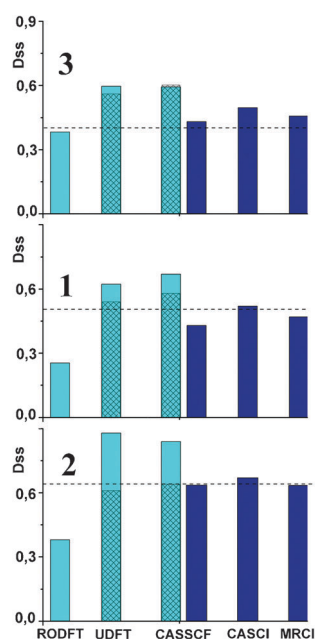

Fig. 5 Calculated parameters D_{SS} of carbenes **1**, **2**, and **3** by DFT and *ab initio* methods. Calculations by the McWeeny–Mizuno formalism are light-coloured, by an *ab initio* formalism—dense-coloured. Contributions of the one-center spin–spin interactions are shown with shading. Dashed lines show the experimental values of D from ref. 6d for carbene **2**, from ref. 26 for carbene **3**, and from this work for carbene **1**.

3. The neglect of two-electron spin–spin correlations in the McWeeny–Mizuno based approach can give rise to positive errors in D_{SS}.

Fig. 5 shows the calculated D_{SS} values obtained by various theoretical methods. The RODFT approach predicts correctly this parameter for vinylcarbene **3**. In contrast to **3**, the D_{SS} parameters for **1** and **2** calculated by RODFT approach are strongly underestimated. The most dramatic departure of the calculated D_{SS} values from the experimental data is observed for "hybrid" ethynylvinylcarbene **1**. The RODFT approach predicts $D \approx 0.26$ cm^{-1} *vs.* the experimental $D = 0.505$ cm^{-1}.

When the unrestricted DFT approach had been applied to target molecules, strongly overestimated D_{SS} values ($\sim$30%–40%) were obtained at this level of theory. The decomposition of the D_{SS} terms into multicenter spin–spin interactions was performed by using the method described in the literature.[14] One-center interactions are dominant as shown in Fig. 5.

E. *Ab initio* calculations of the ZFS parameters

Fig. 5 summarizes the calculated D_{SS} parameters, obtained with both DFT and *ab initio* treatments. It demonstrates that *ab initio* calculations improve considerably predictions of D relative to the experimental values for **1** and **2**. A perfect agreement is achieved for ethynylcarbene **2**, where the errors do not exceed 5%. The D value of ethynylvinylcarbene **1** is underestimated and the D value of vinylcarbene **3** is over-estimated approximately by 20% in both cases.

To check the performance of the McWeeny–Mizuno equation for target molecules, the parameters D_{SS} have been calculated by the McWeeny–Mizuno equation approach using the spin density matrices obtained from CASSCF wave functions (see Fig. 5). The calculations by this method demonstrate strong overestimation, $\sim$30%. The calculated parameters D_{SS} are obtained very close to those calculated by a UDFT + McWeeny–Mizuno approach. This fact allows us to conclude that systematic overestimations in UDFT calculations appear mainly due to the neglect of spin–spin correlation in the McWeeny–Mizuno based approach, whereas the electron spin distributions obtained in UDFT and *ab initio* calculations are nearly the same (Table 1).

Experimental data for **1** and **2** show very low ratio $E/D < 10^{-2}$ which makes accurate theoretical predictions of the parameter E problematic. In addition, experimental values of the para-meter E for molecules with near linear geometry, such as **2**, are subjected to partial averaging due to the high amplitude librational motions about the long axis of the molecule.[6d] However, our calculations (see Table 1) correctly predict the experimental relation $E(2) < E(1) < E(3)$.

F. Electron spin density distributions in carbenes **1**, **2**, and **3**

The calculated singly occupied molecular orbitals (SOMO's) and electron spin distributions in the targeted carbenes are shown in Fig. 6. As an example, a typical electron spin density on the carbenic atom in triplet methylene bearing ortho-gonal π- and σ-electrons is also shown. The electron spin populations on carbon atoms in carbenes **1**, **2**, and **3** are given in Table 1.

Table 1 Calculated ZFS parameters (only spin–spin coupling) and Mulliken spin populations (ρ) of carbenes **1** (C_7H_8), **2** (C_3H_2) and **3** ($C_3H_2Me_2$). The numbering of carbon atoms shown in Fig. 3

Parameter[a]/carbene	**1** (C_7H_8)	**3** ($C_3H_2Me_2$ s-E)[f]	**2** (C_3H_2)
D_{SS}/cm^{-1} (RODFT/UDFT/CAS)	0.26/0.61/0.56	0.39/0.56/0.43	0.39/0.84/0.68
D(exp.)/cm^{-1}	**0.505**[b]	**0.412**[c]	**0.678**[d]
E_{SS}, cm^{-1} (RODFT/UDFT/CAS)	0.011/0.029/0.026	0.028/0.048/0.029	0.004/0.005/0.002
E(exp.)/cm^{-1}	**0.0045**[b]	**0.024**[c]	**0.001**[d]
$|E/D|$(exp.)	**0.009**[b]	**0.058**[c]	**0.0015**[d]
ρ(C1) (RODFT/UDFT/CAS)	0.55/0.86/0.64		0.95/1.24/1.17 (1.24)[e]
ρ(C2) (RODFT/UDFT/CAS)	0.04/−0.34/−0.25		0.07/−0.42/−0.32 (−0.40)[e]
ρ(C3) (RODFT/UDFT/CAS)	1.03/1.24/1.35	1.45/1.63/1.61	0.95/1.24/1.17 (1.24)[e]
ρ(C4) (RODFT/UDFT/CAS)	0.01/−0.22/−0.16	0.04/−0.25/−0.18	
ρ(C5) (RODFT/UDFT/CAS)	0.26/0.42/0.37	0.35/0.54/0.54	

[a] DFT data were obtained at PBE/TZVP level of theory; CAS calculations are based on a T1S2 reference wave function with SVP basis set. [b] This work. [c] From ref. 26. [d] From ref. 6d. [e] Mulliken spin populations obtained in ref. 6c at a QCISD/6-311 + G(2df,p) level are given in brackets. [f] CAS data for carbene **3** were calculated without taking into account CI.

The SOMO's plots in Fig. 6 demonstrate that unpaired electrons in **1** and **2** are delocalized in the orthogonal planes over several carbon atoms. The presence of two electrons on the carbon atoms C1 and C3 ensure the carbenic nature of spin density on these atoms. In addition, the spin density plots show a considerable amount of negative spin density on the carbon atom C2 of **1** and **2**, indicating the "carbenic" character of this atom as well. This feature was predicted earlier in ref. 11 and confirmed experimentally in ref. 6d for **2**. The calculated spin populations in **2** (see Table 1 for UDFT and *ab initio* methods) are in good agreement with those obtained in ref. 6d at the QCISD level. The QCISD calculations were confirmed experimentally by measurements of the hyperfine constants on the carbon ^{13}C. The one-center spin–spin interactions on atoms C1, C2 and C3 give a dominant contribution to the parameter D_{SS} in **1** and **2**. In fact,

if we apply the calculated spin populations on carbon atoms (see Table 1) to eqn (1), the calculated D_{SS} values will be in close agreement with the experimental D values of **1** and **2**: $D_1 \approx D_{CH_2} \times [(\rho_{C1}/2)^2 + \rho_{C2}/2)^2 + (\rho_{C3}/2)^2] = 0.48$, $D_2 \approx D_{CH_2} \times [(\rho_{C1}/2)^2 + \rho_{C2}/2)^2 + (\rho_{C3}/2)^2] = 0.58$.

As follows from Fig. 6 and Table 1, *ca.* 50% of electron spin density of unpaired π-electron in vinylcarbene **3** is localized on carbon atom C5. Weak negative spin density of p-type appears on the carbon C4 ($\rho_4 \approx -0.20$). Both these components do not contribute to the one-center spin–spin interactions. The largest local spin population in carbene **3** is located on the carbon C3, indicating the carbenic nature of its spin density. As it can be seen from Table 1, the spin populations on the atom C3 calculated by different methods (RODFT, UDFT, and *ab initio*) are very close. This fact means that the spin-polarization effects are unimportant for the carbenic atom C3, and that
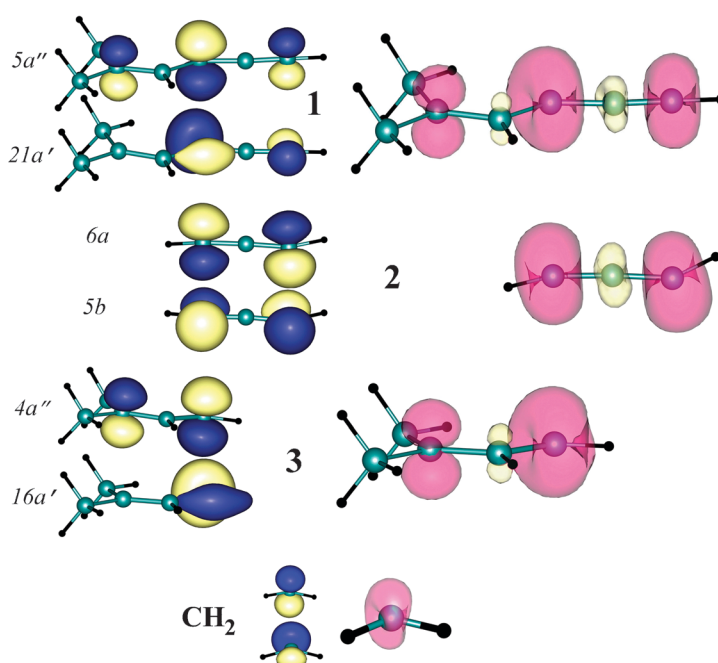

Fig. 6 Calculated by the CASCI method singly occupied molecular orbitals (left) and electron spin density distributions with an isovalue of 0.0125 a.u. (right) in carbenes **1**, **2**, and **3**. Negative spin density shown in light colour. Similar plots for triplet methylene (CH_2) are shown as an example.

one-center spin–spin interactions on this atom provide the dominant contribution to the parameter D_{SS} of **3**.

The "hybrid" ethynylvinylcarbene **1** demonstrates typical features for parent carbenes **2** and **3**. Since carbene **1** has the most delocalized unpaired electrons, its carbon atoms bear the lowest spin densities. Due to this effect, the parameter D_{SS} of **1** is smaller than that in **2**. On the other hand, strong spin polarization in **1** provides higher value of D_{SS} relative to that in vinylcarbene **3**.

G. The ZFS parameters and electron spin distributions in related carbenes

We verified the performance of the most successful CASCI method in predictions of the ZFS parameters for other highly delocalized chain carbenes, such as pentadiynylidene HC_5H (**6**) and cyanocarbene HCCN (**7**). Geometries of these carbenes were taken from ref. 10a and 28: CCSD(T)/cc-pTZ for **6** and CASSCF/aug-cc-pVTZ for **7**.

The calculated parameters D of **6** and **7** are shown in Fig. 4 by reference to the experimental data. Fig. 4 demonstrates that accurate theoretical predictions are obtained for both carbenes. The calculated electron spin densities in carbene **6** (see Fig. 7) indicate the carbenic nature of all carbon atoms. This fact is manifested in a large magnitude of the parameter $D = 0.618$ cm^{-1}. The calculated spin populations are in agreement with previous calculations at the CCSD(T)/

cc-pVTZ level.[10a] Table 2 shows the greatest spin population on the central carbon C3.

Cyanocarbene **7** possesses the greatest parameter $D = 0.822$ cm^{-1} among the carbenes considered. As follows from Fig. 7, configurations of electron spin density on the terminal carbon and nitrogen atoms correspond to the carbenic and nitrenic centers, respectively. Though the most part of spin density occupies carbon C1 ($\rho(C1) = 1.668$), the contribution of the nitrogen atom to the parameter D is significant due to two factors. First, the one-center spin–spin interaction on the nitrogen atom is much greater than that on the carbon atom at identical spin populations.[13g,14c,21] Second, the nitrogen atom introduces an appreciable contribution of the spin–orbit interaction to the parameter D. The calculated spin–orbit coupling $D_{SOC} \approx 0.08$ cm^{-1} in cyanocarbene **7** is much greater than that in carbenes **1–3** and **6**.

Conclusions

The multireference *ab initio* methods are necessary for precise calculations of the ZFS parameters of delocalized carbenes/biradicals. Though UDFT and *ab initio* calculations predict very similar spin populations on carbenic atoms, the UDFT approach in combination with the McWeeny–Mizuno equation overestimates the calculated parameters D by ~30%–40%.

The ESR spectrum of the first representative of "hybrid" ethynylvinylcarbenes, 5-methylhexa-1,2,4-triene-1,3-diyl (**1**), was recorded in a solid argon matrix. The ZFS parameters of **1** were derived from the recorded ESR spectrum with high accuracy. The parameters D and E of **1** fall between the parameters of the parent highly delocalized carbenes, ethynylcarbene HC_3H (**2**) and vinylcarbene $(Me)_2CC(H)CH$ (**3**): $D(3) < D(1) < D(2)$ and $E(2) < E(1) < E(3)$. The main features of electronic structures of **1** are as follows:

1. Unpaired electrons are more delocalized in **1** than in **2** and **3**.

2. Electronic structure of **1** includes the main features of electronic structure of both ethynyl- (**2**) and vinyl- (**3**) carbenes.

3. Magnetic spin–spin interactions are identical in carbenes **1** and **2**. The dominant contribution to the parameter D in **1** and **2** results from the one-center spin–spin interactions on carbon atoms in the propynylidene group, which is subjected to strong spin polarization. The carbenic nature of the electron spin density was revealed for all three carbon atoms in the propargylenic group. Both terminal carbons possess high positive electron spin density, whereas negative spin density is induced on the central carbon atom.

The accurate theoretical predictions of the parameter D are obtained for other types of highly delocalized carbenes, such as HC_5H and HCCN. As in **1–3**, the dominant contribution to the parameter D results from the one-center interactions on the carbenic and nitrenic centers.
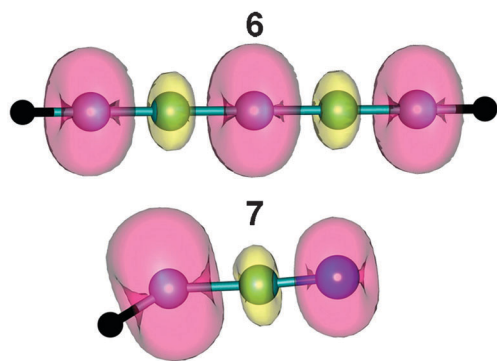

Fig. 7 Calculated electron spin density distributions (CASCI) in carbenes **6** (HC_5H) and **7** (HCCN) with an isovalue of 0.0125 a.u. Negative spin density shown in light colour.

Table 2 Calculated ZFS parameters and spin populations (ρ) of carbenes **6** (HC_5H) and **7** (HCCN)

	Carbene	
Parameter[a]	**6** (HC_5H)	**7** (HC_2N)
D(calc.)/cm^{-1}	0.6176	0.8219
D(expt.)/cm^{-1}	0.6157[b]	0.8629[c]
E(calc.)/cm^{-1}	0.000	0.0002
E(expt.)/cm^{-1}	0[b]	0[c]
ρ(C1–terminal)	0.720 (0.781)[d]	1.668
ρ(C2)	−0.253 (−0.307)[d]	−0.235
ρ(C3–central) in **6**	1.106 (1.102)[d]	
ρ(N)–in **7**		0.545

[a] CAS calculations are based on a T1S2 reference wave function with SVP basis set. [b] From ref. 10a. [c] From ref. 27. [d] Mulliken spin populations obtained in ref. 10a at a CCSD(T)/cc-pVTZ level are given in brackets.

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