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The electronic structure of 5-methylhexa-1,2,4-triene-1,3-diyl, the first representative of highly delocalized triplet ethynylvinylcarbenes, from ESR spectroscopy data and quantum chemical calculations

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The ESR spectrum of the first representative of highly conjugated triplet ethynylvinylcarbenes, 5-methylhexa-1,2,4-triene-1,3-diyl (**1**), was recorded in solid argon matrix. The zero-field splitting (ZFS) parameters of carbene **1** ($D = 0.5054\pm0.0006$ cm^{-1} and $E = 0.0045\pm0.0002$ cm^{-1}) determined from the experimental ESR spectrum are in between the corresponding parameters of ethynylcarbene C_3H_2 (**2**) and vinylcarbene C_3H_4 (**3**): $D(\mathbf{3}) < D(\mathbf{1}) < D(\mathbf{2})$ and $E(\mathbf{2}) < E(\mathbf{1}) < E(\mathbf{3})$. Quantum chemical calculations of the ZFS parameters of **1**, **2**, and **3** have been carried out for the first time using two DFT-based approaches, RODFT and UDFT. An analysis of the experimental and theoretical ZFS parameters shows that carbene **1** is characterized by a greater extent of delocalization of the spin density of unpaired electrons than carbenes **2** and **3**. The characteristic structural fragments of carbene **1** possess the principal features of the electronic structure of both ethynylcarbene (**2**) and vinylcarbene (**3**), respectively. Magnetic spin-spin interactions are identical in carbenes **1** and **2**. The dominant contribution to D in **1** and **2** results from the one-center spin-spin interactions on carbon atoms in the propynylidene group, which are subjected to strong spin polarization.

Key words: carbenes; matrix isolation, ESR spectroscopy, zero-field splitting tensor, electronic spin-spin interactions, quantum chemical calculations, density functional theory.

The existence of vinyl-[1] and ethynylcarbenes[2] was established in the early 1960s already. Later on, the importance of this type intermediates in various chemical reactions and processes,[3—8] including such widespread ones as combustion of hydrocarbon fuels,[9,10] was ascertained. In addition ethynylcarbenes were revealed in interstellar space.[11—14] Nevertheless, some fundamental questions related to interpretation and prediction of chemical properties of these conjugated carbenes based on the characteristics of their molecular and electronic structure and also associated with correct description of their electronic structure itself are still under discussion. For instance, the electronic and spatial structures of the key carbenes like ethynylcarbene C_3H_2,[15—17] vinylcarbene C_3H_4,[18,19] and diethynylcarbene C_5H_2 (see Refs 20—22) had got their final understanding only in the beginning of this century on the basis of studies with the use of low-temperature matrix isolation technique in combination with UV, FTIR, and ESR spectroscopies and modern high-level quantum chemical calculations. All of these carbenes have triplet ground state and are characterized by substantial delocalization of unpaired electrons and strong spin polarization. These features of their electronic structure made it possible to account for some specific chemical properties and magnetic characteristics of these and related intermediates. Recently, we succeeded in stabilization of 5-methylhexa-1,2,4-triene-1,3-diyl (**1**), a new "hybrid" carbene containing fragments of both ethynylcarbene **2** and vinylcarbene **3** in its structure (Scheme 1), in a low-temperature argon matrix and studied it by FT IR spectroscopy.[23]

Density functional calculations[23] at the PBE/TZ2P and B3LYP/6-31G(d) levels of theory gave a set of fundamental frequencies of carbene **1** which were in good agreement with the experimentally observed ones, thus additionally confirming the identity of the observed species. It was established that **1** easily reacts with molecular oxygen in the argon matrices at $T = 12$ K, both terminal carbon atoms of the propynylidene fragment showing approximately equal reactivity as is typical of ethynylcarbenes. However, rearrangements of **1** under UV irradiation result in two major singlet products typical of vinylcarbene rearrangements. These facts indicate a substantial delocaliza-

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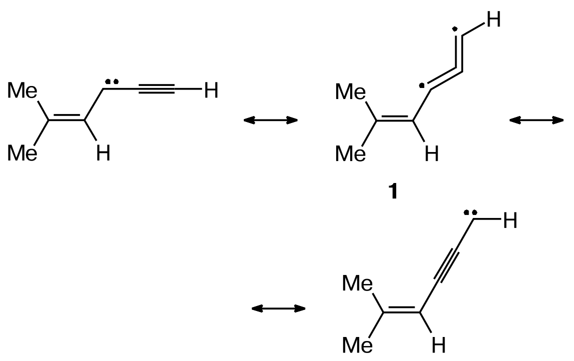
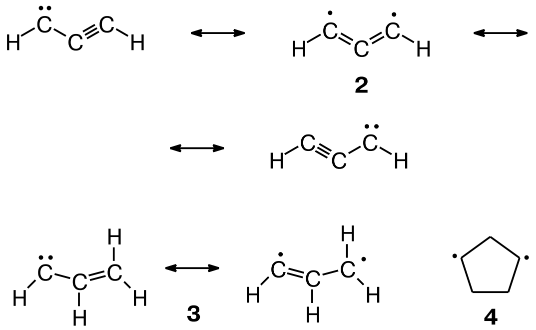
Scheme 1



Scheme 2



tion of unpaired electrons, which determines a carbene-like reactivity of the terminal carbon atoms of the propynylidene fragment, on one hand, and a partially radical nature of the terminal carbon atom of the vinyl group typical of vinylcarbenes, on the other hand.

The present study is devoted to the analysis of the electronic structure of carbene **1** with the use of ESR spectroscopy and quantum chemical calculations. The former method is traditionally employed for unambiguous identification of triplet carbenes characterized by the zero-field splitting (ZFS) parameter $D < 1$ cm^{-1} (see Ref. 24) and for ascertainment of their electronic structure. In the case of carbenes, the scalar parameters D and E of the ZFS tensor are determined by the magnitude of anisotropic magnetic interactions between electron spins of two unpaired electrons. Since magnetic dipole-dipole interactions depend on the relative orientation and distance between the dipoles, the D and E parameters represent precise spectroscopic characteristics of triplet molecules, reflecting spatial distribution of the unpaired electrons and showing the pattern of their delocalization within the molecular structure. The value $D_{CH_2} = 0.74$—0.78 cm^{-1} in triplet methylene[25,26] is considered as a reference parameter characterizing the maximum spin density of two unpaired electrons on a carbene center. This parameter is appreciably smaller for triplet vinylcarbene[27] **3** ($D = 0.409$ cm^{-1}) due to displacement of the spin density of one unpaired electron from the carbene center to the opposite terminal carbon atom in the C_3 chain. A considerably smaller value of $D = 0.08$ cm^{-1} was obtained for diradical cyclopenta-1,3-diyl (**4**)[28] in which two unpaired electrons are localized on different carbon atoms (Scheme 2).

In the parent ethynylcarbene, propynylidene HCCCH (**2**), both unpaired electrons are equally delocalized over two terminal carbon atoms, and this distribution determines a typical carbene pattern of interactions of these atoms with various reactants. Nevertheless, despite such a high degree of delocalization of the spin density, the D parameter for this carbene[17] ($D = 0.64$—0.65 cm^{-1}) is only ~15% smaller than the maximum value D_{CH_2}. It was supposed[29] that such a high value is due to spin polarization, which leads to the appearance of negative electron spin density of the carbene type on the central carbon atom and additionally contributes to the D parameter. This phenomenon found its experimental corroboration[17] only in 2009 in an ESR study of matrix-isolated ^{12}C/^{13}C-isotopomers of HCCCH.

Here we report the first experimentally observed ESR spectrum of matrix-isolated carbene **1** and the derived ZFS parameters of this species. The latter have been used to test capability of DFT calculations in prediction of the parameters of triplet carbenes. Based on the experimentally obtained parameters and results of quantum chemical calculations, the spin density distribution of the unpaired electrons in **1** was characterized and the electronic structure of **1** was compared with those of **2** and **3**.

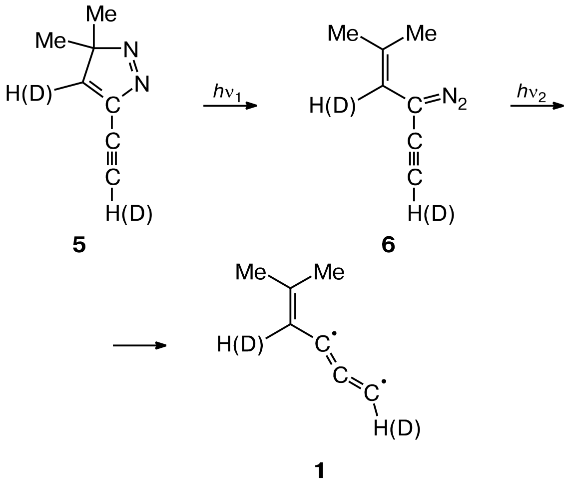
Experimental

5-Methylhexa-1,2,4-triene-1,3-diyl **1** was generated in solid argon as described earlier.[23] 3,3-Dimethyl-5-ethynyl-3*H*-pyrazole (**5**), a precursor of carbene **1**, was synthesised according to the published method.[30] The identity of 3*H*-pyrazole **5** was confirmed using ^{1}H NMR ($CDCl_3$, a Bruker AC-200P spectrometer) and IR spectroscopies (KBr pellets, a Bruker IFS 113v spectrometer), the purity of the sample was controlled by GLC.

The cryogenic apparatus and the procedure of the ESR measurements were described in detail previously.[31,32] Thin films of argon matrices doped with 3*H*-pyrazole **5** were obtained by vacuum co-deposition of molecular beams of argon and 3*H*-pyrazole, issued from two separated nozzles, on the bottom end of a flat sapphire rod, positioned inside a helium cryostat and held at 15 K. The molecular beam of compound **5** was formed by sublimation of the sample from a glass ampoule at room temperature, its intensity was controlled with teflon valve and verified by a PMT-2 thermocouple gauge. In preliminary experiments, a regime was selected that ensured an optimal deposition rate of **5** to attain the ratio Ar : **5** ≈ (10^3—10^4) : 1. The film thicknesses were at most 150 μm. After deposition, the sapphire rod was descended to the center of the ESR cavity. Photolysis of the matrix was carried out at 15 K through an aperture in the cavity using a low-pressure Hg lamp (Mercury Spectral Line Lamp, Lot-Oriel) equipped with narrow band interference filters (Lot-

Oriel, half band widths of ~5 nm). Matrix isolated 3*H*-pyrazole **5** was initially irradiated with light at 365 nm until the appearance of the ESR lines of **1** and then with light at 297 nm. This irradiation sequence corresponds to previously revealed[23] two-step transformation of **5** into **1** *via* intermediate 3-diazo-5-methylhex-4-en-1-yne (**6**) (Scheme 3).

Scheme 3



The same irradiation sequence was repeated using the equipment with IR detection employed in the previous study,[23] and predominant formation of **1** was detected at that, thus confirming suitability of this procedure. Carbene **1** could also be obtained by photolysis of **5** at 365 nm, but its yield was several times lower.

ESR spectra of matrices held at 15 K were recorded with an X-band ESR spectrometer (Radiopan, Poland) maintaining microwave power and modulation amplitude sufficiently low to avoid the saturation effects.

Computer simulations of powder ESR spectra were performed using the EasySpin program package[33] which employs an exact numerical matrix diagonalization analysis of the spin Hamiltonian (1):

$$H = g\beta HS + S\hat{D}S, \quad (1)$$

where $\hat{D}$ is the ZFS tensor characterized by two scalar parameters D and E, $S = 1$, β is the electron Bohr magneton, and g is the electron g-factor.

The parameters of spin-spin interactions were calculated according to the McWeeny—Mizuno equation[34] using two DFT approaches, *viz.*, (1) restricted open-shell DFT (RODFT) and (2) unrestricted DFT (UDFT); the calculations were performed using the ORCA program package.[35] Both approaches have some limitations in evaluation of two-electron (spin-spin) interactions due to fundamental concepts underlying these approaches. The UDFT approach is subject to the spin contamination effect consisting in an excess of the calculated spin momentum over the nominal value due to coupling with excited electronic states with multiplicity higher than 1, i.e., the expectation value $\langle S^2 \rangle$ is larger than S(S + 1), the exact value for the multispin states. Because the spin-spin interaction energy is a function of the total electron spin operator S^2, this effect represents a main source of inaccuracy of the UDFT calculations, which results in overestimation of the *D* parameter. The expression $\langle S^2 \rangle = S(S + 1)$ is strictly fulfilled in the RODFT approach. However, spin polarization effects are not reproduced by RODFT. Thus, a correct spin density distribution cannot be obtained within this approach for molecules with strong spin polarization. Applicability of the RODFT and UDFT approaches to the calculations of the *D* and *E* parameters of a number of triplet inorganic and organic molecules[36,37] and high-spin nitrenes of the pyridine series[38] was tested with the use of the ORCA program package. It was shown that the accuracy of calculation of *D* parameters within the RODFT approach is 5—20% for organic triplet biradicals ($D \approx 0.02$—0.08 cm^{-1}) and triplet carbenes of the phenyl and diphenyl series ($D \approx 0.5$—0.3 cm^{-1}). On the contrary, in the case of high-spin nitrenes of the pyridine series, the same accuracy is achieved within the UDFT approach, whereas RODFT calculations give much larger errors. None of these approaches has been applied so far to describe the ZFS parameters of conjugated triplet carbenes like **1**—**3**. In the present work, we have tested both DFT approaches in calculations of the ZFS parameters of systems **1**—**3** using the PBE functional and several basis sets (EPRIII, EPRII, TZVPP, TZVP, TZV, DZP, DZ), which gave good results in the previous studies.[36—38] Optimization of structures **1**—**3** was carried out at the complete active space SCF (CASSCF) level of theory with the three-exponential basis set TZVP[39] augmented with a set of polarization functions. The active space for carbene **1** included eight π-type molecular orbitals (MOs) and eight electrons participating in delocalization of the electron and spin densities (hereafter designated as (8,8)). CAS(6,6) and CAS(4,4) active spaces were used in the CASSCF structure optimization of carbenes **2** and **3**, respectively.

Results and Discussion

The ESR spectrum and zero-field splitting parameters of triplet carbene 1. Photolysis of 3*H*-pyrazole **5** isolated in solid argon results in the appearance of an ESR spectrum typical of randomly oriented triplet molecules with 0.3 cm^{-1} < D < 1 cm^{-1}.[40] The ESR spectrum shown in Fig. 1 exhibits characteristic lines, which are distinctive for this type of high-spin molecules. Two side bands (at resonance fields z_1 of 215.5 mT and z_2 of 865.6 mT) correspond to the allowed transitions with $\Delta m_s = \pm 1$ in molecules with parallel orientation of the easy axis relative to the direction of the external magnetic field (**H**||**Z**), while the middle line (x_1 at 521.3 mT and y_1 at 539.6 mT) corresponds to the perpendicular orientation (**H**⊥**Z**). The doublet splitting of the perpendicular line indicates a nonzero value of the *E* parameter ensuring the spectral resolution of two components with the canonical orientations, **H**||**X** and **H**||**Y**, in the powder spectrum (here **X**, **Y** and **Z** are principal axes of the tensor **D**).

The zero-field splitting parameters *D* and *E* were obtained by fitting the simulated powder ESR spectrum to the experimental ESR spectrum. The lines were assumed to be Gaussians with variable band halfwidth. The procedure for evaluation of the *D* and *E* parameters and error estimation for these quantities were described in details earlier[41]. To obtain true values of the ZFS parameters, the

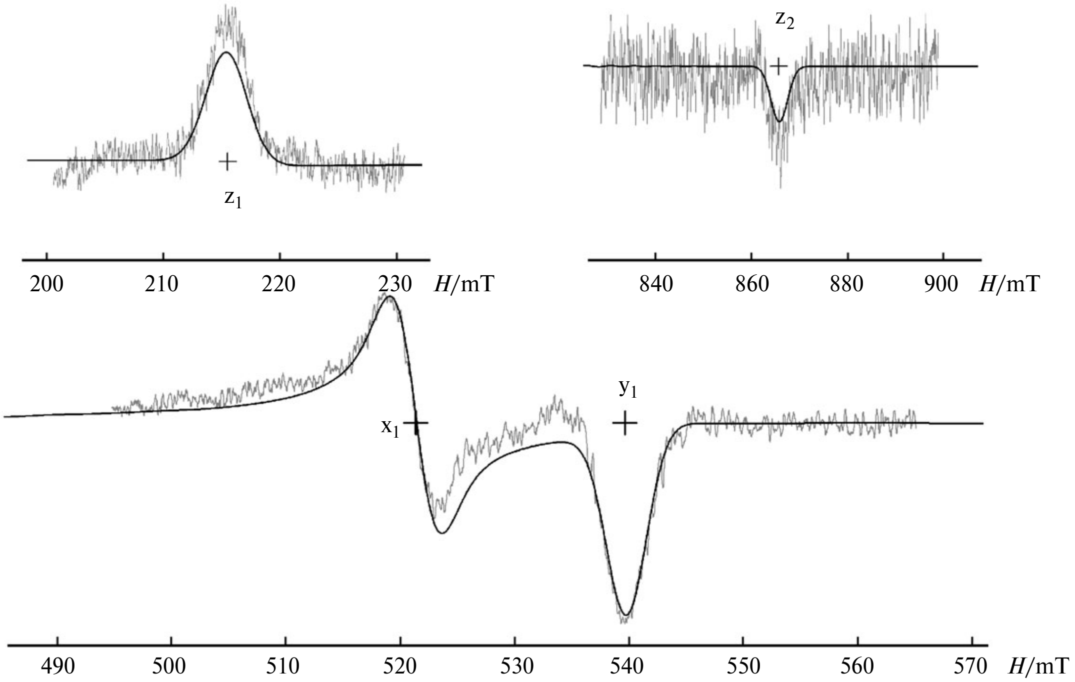


Fig. 1. ESR spectrum of a triplet species formed upon photolysis of **5** isolated in an argon matrix at 15 K. The simulated spectrum with the zero-field splitting parameters $D = 0.5054$ cm^{-1} and $E = 0.0045$ cm^{-1} is shown by the solid line. The resonance magnetic fields of the four lines are marked with "+". The microwave frequency is 9.112447 GHz.

D and *E* parameters were varied to minimize the *R* functional equal to the root-mean-square deviation of the calculated resonance fields from their experimentally measured values:

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

where *n* is the number of spectral lines used. The resonance fields of the experimentally observed lines are marked in Fig. 1. The z$_2$ line of low intensity was not used in the *R* minimization because the accuracy of its resonance field measurement was significantly lower than for other three lines.

The best fit shown in Fig. 1 corresponds to the minimum value of $R = 0.02$ mT and the parameters $D = 0.5054 \pm 0.0006$ cm^{-1} and $E = 0.0045 \pm 0.0002$ cm^{-1}. The errors of the *D* and *E* parameters were obtained from the *R* functional variations depending on the variations of the *D* and *E* parameters in the vicinity of their optimal values. The value $R = 3.5$ mT equal to the line halfwidth in the experimental spectrum was used as a critical value for the functional variation.

The fact of detection of the ESR spectrum of a triplet intermediate upon photolysis of matrix isolated 3*H*-pyrazole **5** is a direct experimental verification of the main conclusion of the previous study[23], where the conclusion about stabilization of triplet ethynylvinylcarbene **1** was made on the basis of IR spectroscopic measurements. According to our data, the *D* parameter of carbene **1** falls between the corresponding values for vinylcarbene and ethynylcarbene: $D(\mathbf{3}) < D(\mathbf{1}) < D(\mathbf{2})$.

Calculations of the zero-field parameters for carbenes 1—3. The calculated structural parameters of carbene **1** (Fig. 2) are close to those obtained earlier[23] at the PBE/TZ2P level of theory.

The calculated spin density distribution of unpaired electrons in carbene **1** is shown in Fig. 3. The inset in Fig. 3 demonstrates the spin density distribution in triplet methylene formed by orbitals of two unpaired electrons localized on the carbon atom. In carbene **1**, the carbene-like configuration of the spin density (ρ) is present at the

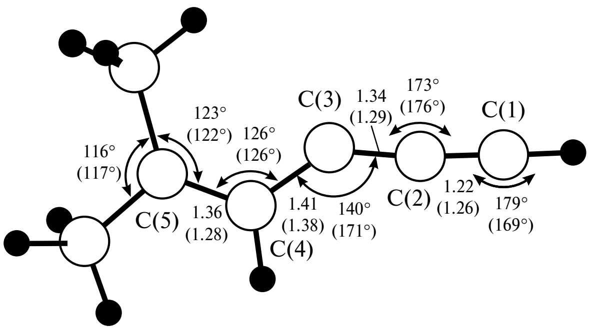


Fig. 2. Bond lengths (in Å) and bond angles (in degrees) in carbene **1** according to the CASSCF(8,8)/TZVP and UDFT PBE/TZ2P[23] calculations (numbers in parentheses).

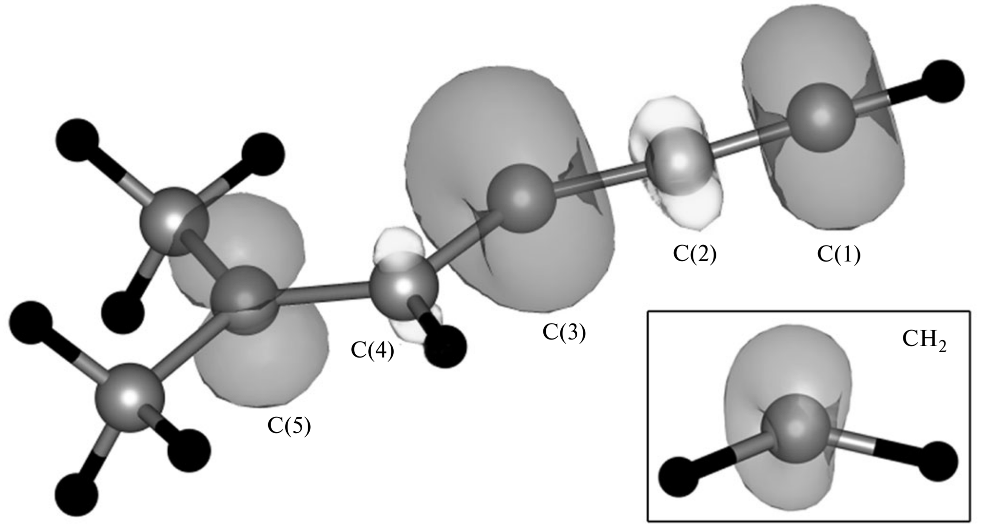


Fig. 3. Electron spin density distribution in carbene **1** according to the UDFT PBE/TZVP calculations. The negative spin density on the C(4) and C(2) atoms is shown in pale grey. Inset: spin density distribution on the carbon atom of triplet methylene.

C(1) and C(3) atoms: $\rho(C(1)) = 0.86$, $\rho(C(3)) = 1.24$, these figures are similar to the values for ethynylcarbene **2**: $\rho(C(1)) = \rho(C(3)) = 1.24$ (Table 1). Also, similar negative spin density is induced on the C(2) atoms of carbenes **1** and **2**: $\rho(C(2)) = -0.34$ and -0.42, respectively. Similarly to vinylcarbene **3**, in which substantial spin density of one of the unpaired electrons is transferred to the terminal carbon atom of the vinyl group (this atom corresponds to the C(5) atom in **1** and will be designated below as C(5)): $\rho(C(5)) = 0.63$, carbene **1** is also characterized by substantial spin density on the C(5) atom: $\rho(C(5)) = 0.42$. Thus, the main structural moieties of **1** have some electronic structure features characteristic of ethynylcarbene **2** and vinylcarbene **3**.

The zero-field splitting parameters *D* of carbenes **1**—**3** calculated by different DFT methods are depicted in Fig. 4. The RODFT results demonstrate that taking into account only α-electrons gives the lowest value of the *D* parameter for **1**. This fact reflects the higher degree of delocalization of unpaired electrons in this carbene as compared to carbenes **2** and **3**. The one-center interactions of two unpaired electrons make a dominant contribution to the *D* parameters as shown in Fig. 4. The RODFT calculated values of the *D* parameters of carbenes **1**—**3** are close to the values estimated by the Wasserman semiempirical equation[29] for one-center spin-spin interactions:

$$D_{C_3H_4} \approx D_{CH_2} \cdot [\rho_{C(3)}/2]^2 = 0.43,$$

$$D_{C_3H_2} \approx D_{CH_2} \cdot [(\rho_{C(1)}/2)^2 + (\rho_{C(3)}/2)^2] = 0.37,$$

$$D_{C_7H_8} \approx D_{CH_2} \cdot [(\rho_{C(1)}/2)^2 + (\rho_{C(3)}/2)^2] = 0.26.$$

The RODFT calculations of the *D* parameter of vinylcarbene **3**, as well as its estimation by the Wasserman equation are in good agreement with the experimental data (accuracy is ±10%). Thus, the spin polarization effects are insignificant in this species. A different situation is in the case of carbenes **1** and **2**. As it is seen from Fig. 4, the RODFT calculations considerably underestimate the *D* parameters of these carbenes. This result is rather expected as the spin polarization effects are responsible for the high value of the *D* parameter of ethynylcarbene **2** (see Refs 17, 29).

The UDFT calculations result in correct sequence of the *D* values for the carbenes under consideration: $D(\mathbf{3}) < D(\mathbf{1}) < D(\mathbf{2})$, although the calculated values are overestimated as compared to experimental ones in all the cases. In accordance with the RODFT data for vinylcarbene **3**, it is expected that taking into account of the spin polarization by the UDFT approach should not result in considerable changes in the *D*(**3**) parameter. Indeed, the values of spin density on the C(3) atom in **3** calculated by two methods (Table 1) indicate that the contribution of the one-center interaction to the *D*(**3**) parameter should increase by 20% only when spin polarization effects are taken into consideration. Simultaneously, the increasing spin density on the C(3) and C(5) atoms should result in approximately equal increase in the C(3)—C(5) two-center interaction energy negatively contributing to the *D*(**3**) parameter. Thus, the significant 40—50% overestimation of the *D*(**3**) parameter in the UDFT calculations obviously relates to some feature inherent to this approach and, first of all, to the spin contamination (see above). The UDFT calculations overestimate the *D* parameters of carbenes **1** and **2** by at most 30%. This fact allows one to point out the main factor among spin polarization effects, which is responsible for the increase in the *D*(**1**) and *D*(**2**) parameters. It is the negative spin density on the C(2) atoms of

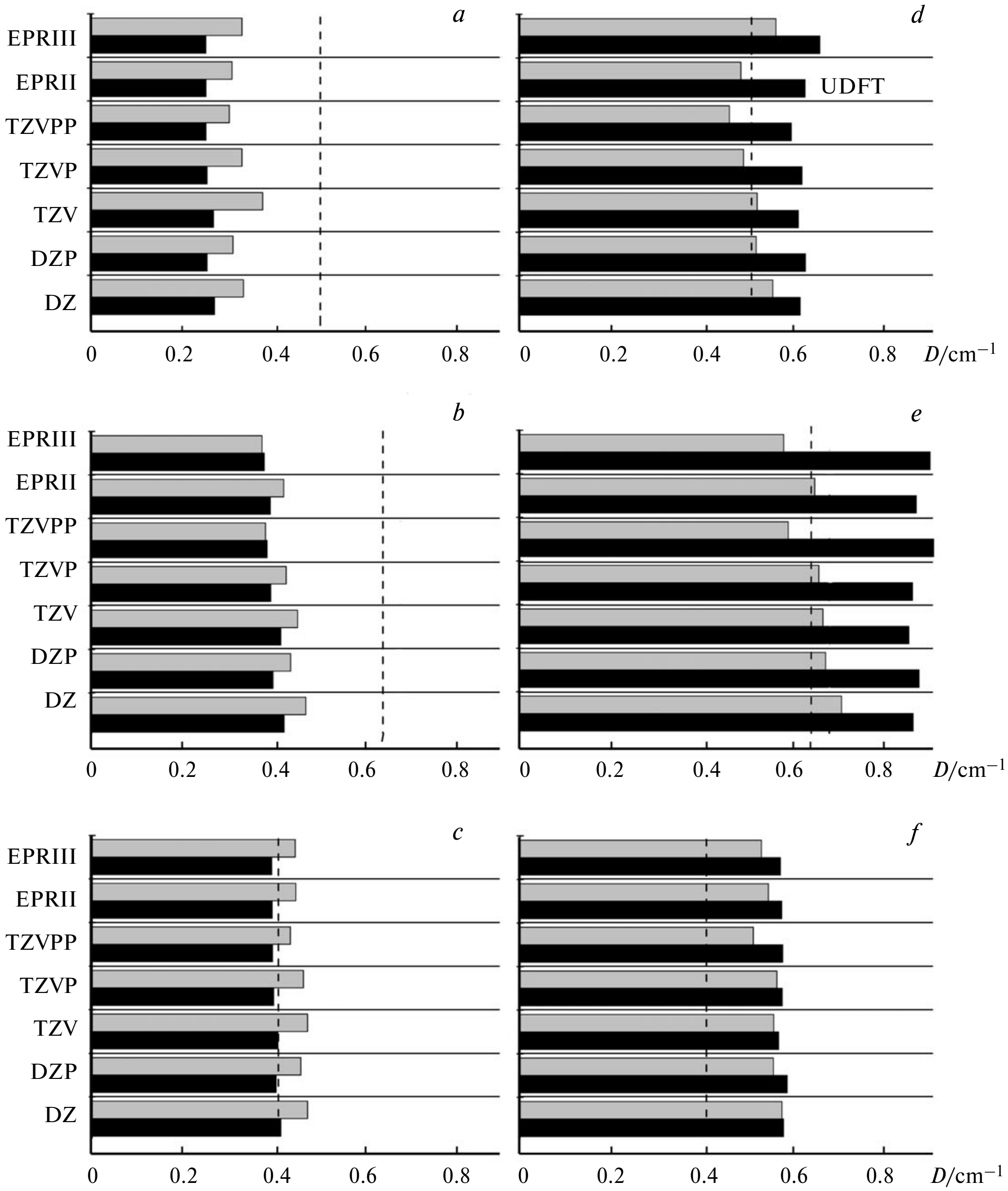


Fig. 4. The RODFT (*a*—*c*) and UDFT (*d*—*f*) calculated *D* parameters of carbenes **1** (*a, d*), **2** (*b, e*) and **3** (*c, f*) (given in black). The vertical dashed lines show the experimental values. The contributions of one-center spin-spin interactions to the *D* parameter are given in grey.

both carbenes. High negative spin density on the C(2) atom in ethynylcarbene **2** was recently revealed experimentally and confirmed in quantum chemical calculations.[17] A comparison of the calculated spin densities on the C(2) atoms in carbenes **1** and **2** indicates that the same effect is operating in **1**. Consideration of spin polarization leads to an increase in the spin density on the C(1) and C(3) atoms, which should result in the 60—70% increase in the one-center interaction energy. In addition, the negative spin density of the carbene type on the C(2) atom provides an additional contribution to the one-center and C(1)—C(2) and C(2)—C(3) two-center interactions. Thus, the results of quantum chemical calculations of the *D* parameters and the spin density distributions in carbenes **1**—**3** clearly testify for identical nature of spin-spin interactions in **1** and **2**. The lower *D*(**1**) value in comparison with *D*(**2**) is caused by partial transfer of spin density of one of electrons to the vinyl group, viz., to the C(5) atom in **1**. This transfer results in some weakening of one-center interactions in **1** as compared to **2**.

Table 1. Calculated and experimental zero-field splitting parameters and spin density (ρ) in carbenes **1**—**3**[a]

Parameter[b]	**1**	**3**	**2**
D/cm^{-1} (UDFT/RODFT)	0.61/0.26	0.58/0.40	0.84/0.39
D_{exp}/cm^{-1}	**0.505**[c]	**0.409**[d]	**0.64—0.65**[e]
E/cm^{-1} (UDFT/RODFT)	0.029/0.011	0.051/0.028	0.005/0.004
E_{exp}/cm^{-1}	**0.0045**[c]	**0.022**[d]	**0.001**[e]
$\lvert E/D\rvert_{\mathrm{exp}}$	**0.009**[c]	**0.054**[d]	**0.0015**[e]
ρ(C(1)) (UDFT/RODFT)	0.86/0.55	—	1.24/0.95 (1.24)[f]
ρ(C(2)) (UDFT/RODFT)	−0.34/0.04	—	−0.42/0.07 (−0.40)[f]
ρ(C(3)) (UDFT/RODFT)	1.24/1.03	1.64/1.47	1.24/0.95 (1.24)[f]
ρ(C(4)) (UDFT/RODFT)	−0.22/0.01	−0.27/0.03	—
ρ(C(5)) (UDFT/RODFT)	0.42/0.26	0.63/0.41	—

[a] The carbon atom numbering scheme is shown in Fig. 3.
[b] Obtained from PBE/TZVP calculations.
[c] This work.
[d] Data taken from Ref.27.
[e] Data taken from Ref.17.
[f] Numbers in parentheses represent the results of QCISD/6-311+G(2df,p) calculations.[17]

The E parameter describes the asymmetry of magnetic interactions in the XY plane perpendicular to the light axis Z. The largest value of this parameter has carbene **3**, for which the ratio $\lvert E/D\rvert = 0.054$ is one of the highest of those known for carbenes[24]. The RODFT calculations reproduce the E and $\lvert E/D\rvert$ values for carbene **3** rather well (Table 1). Molecules **1** and **2** are characterized by lower E values, and the $\lvert E/D\rvert$ ratio is below 0.01 for them. By definition, the E parameter characterizes the difference in magnetic interactions. Therefore, its calculation is difficult when $\lvert E/D\rvert < 0.01$ (see Refs 36, 38). According to the data shown in Table 1, both DFT approaches considerably overestimate this parameter for carbenes **1** and **2**. Nevertheless, the calculations correctly predict the increase in the E value in the series $E(\mathbf{2}) < E(\mathbf{1}) < E(\mathbf{3})$.

An analysis of the experimental ESR data and the results of quantum chemical calculations suggests the following.

The zero-field splitting parameters D and E of triplet carbene **1** obtained from experimental ESR spectra fall between the corresponding values for vinylcarbene **3** and ethynylcarbene **2**: $D(\mathbf{3}) < D(\mathbf{1}) < D(\mathbf{2})$, $E(\mathbf{2}) < E(\mathbf{1}) < E(\mathbf{3})$, and $\lvert E/D\rvert(\mathbf{2}) < \lvert E/D\rvert(\mathbf{1}) < \lvert E/D\rvert(\mathbf{3})$.

In the series of carbenes **1**—**3**, the highest delocalization of the unpaired electron spin density is in carbene **1**; at the same time, the electronic structures of the propynylidene and vinylcarbene structural fragments in carbene **1** closely resemble those of carbenes **2** and **3**, respectively.

The results of theoretical calculations of the zero-field splitting parameters and spin density distributions show that the character of the spin-spin interactions in carbenes **1** and **2** is identical, the electronic structures of these carbenes are characterized by significant spin polarization. The D parameter is predominantly contributed by one-center spin-spin interactions at all of the carbon atoms of the propynylidene group (C(1), C(2) and C(3)) with the carbene-like electronic configurations.

The C(5) atom of the vinyl moiety in carbene **1** bears a rather high spin density of the unpaired p-electron, whose value is close to the spin density value on the corresponding atom in vinylcarbene **3**.

In triplet carbene **3**, the spin polarization effects slightly affect the spin-spin interaction energy. Therefore the RODFT approach reproduces the magnetic parameters of this carbene quite well. On the contrary, the spin polarization in carbenes **1** and **2** significantly affects both the spin density distribution and magnetic spin-spin interactions. As a result, the RODFT approach underestimates (approximately, by 2 times) their D values in comparison with the experimentally obtained ones. Taking into account the spin polarization effects, the UDFT approach results in much better agreement between the calculated and experimental D values of carbenes **1** and **2**, though the calculated values are overestimated by 25—30%. Obviously, the use of high level *ab initio* approaches, which take into account both static and dynamic correlation and have no limitations typical of McWeeny—Mizuno formalism,[42] is required to obtain more precise theoretical results.

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