Supporting Information

Paper:

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

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Content:

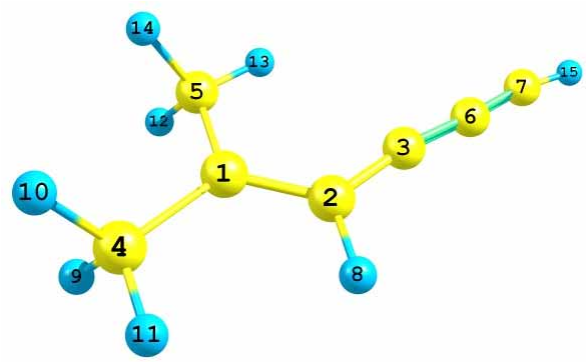
1. **Cartesian coordinates of carbenes under consideration**

1 C_7H_8			Method : CASSCF(8,8)/TZVP Charge : 0 Multiplicity : 3 Symmetry : C_S
6	1.458792000	0.053505000	0.000000000
6	0.204551000	0.587447000	0.000000000
6	-0.997631000	-0.145341000	0.000000000
6	2.674932000	0.939218000	0.000000000
6	1.721196000	-1.427705000	0.000000000
6	-2.328056000	0.053729000	0.000000000
6	-3.556867000	0.085006000	0.000000000
1	0.103246000	1.660742000	0.000000000
1	3.291601000	0.746003000	-0.873621000
1	3.291601000	0.746003000	0.873621000
1	2.410292000	1.989221000	0.000000000
1	2.301794000	-1.710168000	-0.873974000
1	0.807941000	-2.006351000	0.000000000
1	2.301794000	-1.710168000	0.873974000
1	-4.608187000	0.146506000	0.000000000

2 C_3H_2			Method : CASSCF(6,6)/TZVP Charge : 0 Multiplicity : 3 Symmetry : C_2
6	1.239163653	-0.304662729	0.053295474
6	0.000000000	0.000000000	-0.058143924
6	-1.239163653	0.304662729	0.053295474
1	2.231891617	-0.165467875	-0.288425216
1	-2.231891617	0.165467875	-0.288425216

3 $C_3H_2Me_2$			Method : CASSCF(4,4)/TZVP Charge : 0 Multiplicity : 3 Symmetry : C_s
6	-2.079341875	0.127028643	0.000000000
6	-0.803142822	0.687406921	0.000000000
6	0.389512673	0.001928727	0.000000000
1	-3.043692030	0.592842600	0.000000000
1	-0.761156236	1.766624535	0.000000000
6	0.465267329	-1.500323838	0.000000000
1	1.005199177	-1.855703051	0.873896773
1	-0.513613688	-1.959544458	0.000000000
1	1.005199177	-1.855703051	-0.873896773
6	1.704319866	0.731959386	0.000000000
1	2.294392849	0.466648561	0.873568439
1	2.294392849	0.466648561	-0.873568439
1	1.569765785	1.806660427	0.000000000

2. Calculated hyperfine interaction constants (in MHz) in carbene 1 at PBE/EPRII level of the theory.



Nucleus 1C : A:ISTP= 13 I= 0.5 P=134.1900 MHz/au**3
Q:ISTP= 13 I= 0.5 Q= 0.0000 barn

A(Tot) 21.3293 24.4138 77.2481 A(iso)= 40.9970
Orientation:

X	-0.3325208	-0.9430945	0.0016240
Y	-0.9430955	0.3325217	0.0003001
Z	-0.0008230	-0.0014318	-0.9999986

Nucleus 2C : A:ISTP= 13 I= 0.5 P=134.1900 MHz/au**3
Q:ISTP= 13 I= 0.5 Q= 0.0000 barn

A(Tot) -24.9212 -28.2517 -47.9839 A(iso)= -33.7189
Orientation:

X	-0.9985089	-0.0545660	-0.0016167
Y	0.0545665	-0.9985101	-0.0003007

Z -0.0015978 -0.0003885 0.9999986

Nucleus 3C : A:ISTP= 13 I= 0.5 P=134.1900 MHz/au**3
Q:ISTP= 13 I= 0.5 Q= 0.0000 barn

A(Tot) 3.1813 65.0156 84.5415 A(iso)= 50.9128
Orientation:
X -0.9770915 -0.0016036 -0.2128136
Y -0.2128134 -0.0003214 0.9770928
Z -0.0016353 0.9999987 -0.0000273

Nucleus 4C : A:ISTP= 13 I= 0.5 P=134.1900 MHz/au**3
Q:ISTP= 13 I= 0.5 Q= 0.0000 barn

A(Tot) -8.0529 -8.8867 -9.2802 A(iso)= -8.7399
Orientation:
X -0.9147403 -0.0015740 -0.4040393
Y -0.4040395 -0.0002251 0.9147415
Z -0.0015307 0.9999987 -0.0004301

Nucleus 5C : A:ISTP= 13 I= 0.5 P=134.1900 MHz/au**3
Q:ISTP= 13 I= 0.5 Q= 0.0000 barn

A(Tot) -5.7928 -6.2015 -6.9734 A(iso)= -6.3225
Orientation:
X -0.9928654 0.1192295 -0.0016275
Y -0.1192291 -0.9928667 -0.0003258
Z -0.0016548 -0.0001295 0.9999986

Nucleus 6C : A:ISTP= 13 I= 0.5 P=134.1900 MHz/au**3
Q:ISTP= 13 I= 0.5 Q= 0.0000 barn

A(Tot) -37.1382 -67.4798 -68.3617 A(iso)= -57.6599
Orientation:
X -0.9838059 0.0016223 0.1792296
Y -0.1792296 0.0001528 -0.9838073
Z -0.0016235 -0.9999987 0.0001404

Nucleus 7C : A:ISTP= 13 I= 0.5 P=134.1900 MHz/au**3
Q:ISTP= 13 I= 0.5 Q= 0.0000 barn

A(Tot) 8.3829 67.2986 82.7268 A(iso)= 52.8028
Orientation:
X -0.9932274 -0.0016137 -0.1161751

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 Y      -0.1161748   -0.0003060    0.9932287
 Z      -0.0016383    0.9999987    0.0001164
---------------------------------------------------------------
 Nucleus   8H : A:ISTP=    1 I=  0.5 P=533.5514 MHz/au**3
             Q:ISTP=    2 I=  1.0 Q=  0.0029 barn
 ---------------------------------------------------------------
A(Tot)     47.1087      50.0223      55.4157 A(iso)=    50.8489
 Orientation:
 X      -0.0016157    0.2195926    0.9755903
 Y      -0.0002794   -0.9755917    0.2195924
 Z       0.9999987    0.0000822    0.0016376
 RHO(0)=      0.477397914 a.u.**-3
 ---------------------------------------------------------------
 Nucleus   9H : A:ISTP=    1 I=  0.5 P=533.5514 MHz/au**3
             Q:ISTP=    2 I=  1.0 Q=  0.0029 barn
 ---------------------------------------------------------------
A(Tot)     23.4228      23.6975      27.6921 A(iso)=    24.9375
 Orientation:
 X       0.3164224   -0.0333826   -0.9480308
 Y      -0.3857633   -0.9175428   -0.0964464
 Z      -0.8666392    0.3962334   -0.3032089
 RHO(0)=      0.479612131 a.u.**-3
 ---------------------------------------------------------------
 Nucleus  10H : A:ISTP=    1 I=  0.5 P=533.5514 MHz/au**3
             Q:ISTP=    2 I=  1.0 Q=  0.0029 barn
 ---------------------------------------------------------------
 A(Tot)     23.4226      23.6974      27.6918 A(iso)=    24.9373
 Orientation:
 X      -0.3136072   -0.0321979   -0.9490067
 Y       0.3864975   -0.9172174   -0.0966020
 Z      -0.8673351   -0.3970838    0.3000904
---------------------------------------------------------------
 Nucleus  11H : A:ISTP=    1 I=  0.5 P=533.5514 MHz/au**3
             Q:ISTP=    2 I=  1.0 Q=  0.0029 barn
 ---------------------------------------------------------------
A(Tot)     -0.4816      -0.8470       3.0962 A(iso)=     0.5892
 Orientation:
 X       0.6164887   -0.0015697   -0.7873622
 Y      -0.7873634   -0.0003579   -0.6164890
 Z       0.0006859    0.9999987   -0.0014565
---------------------------------------------------------------
 Nucleus  12H : A:ISTP=    1 I=  0.5 P=533.5514 MHz/au**3
             Q:ISTP=    2 I=  1.0 Q=  0.0029 barn
 ---------------------------------------------------------------
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A(Tot) 18.4033 19.4365 22.9834 A(iso)= 20.2744
Orientation:
X 0.1384973 0.8750668 0.4637634
Y -0.3160929 0.4828423 -0.8166692
Z -0.9385647 -0.0334859 0.3434748
RHO(0)= 0.479665250 a.u.**-3

Nucleus 13H : A:ISTP= 1 I= 0.5 P=533.5514 MHz/au**3
Q:ISTP= 2 I= 1.0 Q= 0.0029 barn

A(Tot) -0.2165 -3.2033 4.6853 A(iso)= 0.4218
Orientation:
X -0.8507553 -0.0016108 -0.5255596
Y -0.5255598 -0.0003170 0.8507566
Z -0.0015371 0.9999987 -0.0005769
RHO(0)= 0.483125927 a.u.**-3

Nucleus 14H : A:ISTP= 1 I= 0.5 P=533.5514 MHz/au**3
Q:ISTP= 2 I= 1.0 Q= 0.0029 barn

A(Tot) 18.4034 19.4366 22.9835 A(iso)= 20.2745
Orientation:
X -0.1354863 0.8749483 0.4648753
Y 0.3166639 0.4828319 -0.8164541
Z -0.9388117 0.0365909 -0.3424817

Nucleus 15H : A:ISTP= 1 I= 0.5 P=533.5514 MHz/au**3
Q:ISTP= 2 I= 1.0 Q= 0.0029 barn

A(Tot) -19.9464 -49.5878 -52.0370 A(iso)= -40.5237
Orientation:
X -0.9994483 0.0331716 -0.0016677
Y -0.0331711 -0.9994496 -0.0003427
Z -0.0016781 -0.0002871 0.9999986

3. The accuracy of the measurements of the parameters *D* and *E* of carbene 1.

To estimate an accuracy of *D* and *E* measurements, the rms deviations were calculated by varying each of the parameters close to their optimum values (Figure S1). The rms deviation of *R* = 3.5 mT was chosen as a crucial one, if at least one of the tested lines had deviation $|H(calc) - H(exp)|$ exceeding the line width. This treatment gave the experimental errors for *D* and *E* that were not more than ± 0.0006 and ± 0.0002 cm^{-1}, respectively.

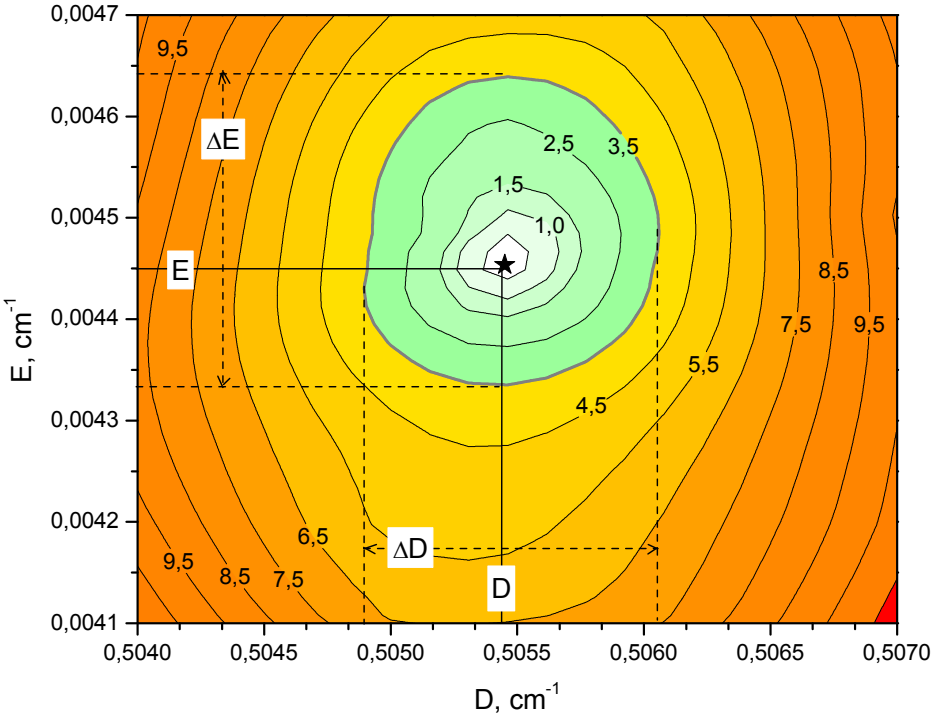

Figure S1. Contour plots of isovalues of the functional *R*. The minimum of *R* (denoted with asterisk) was obtained at *D* = 0.5054 cm^{-1} and *E* =0.0045 cm^{-1}. It corresponds to the rms deviation of *R*(min) = 0.02 mT.

4. Calculated parameters *D* of carbenes 1, 2, and 3 with various basis sets and reference wave functions.

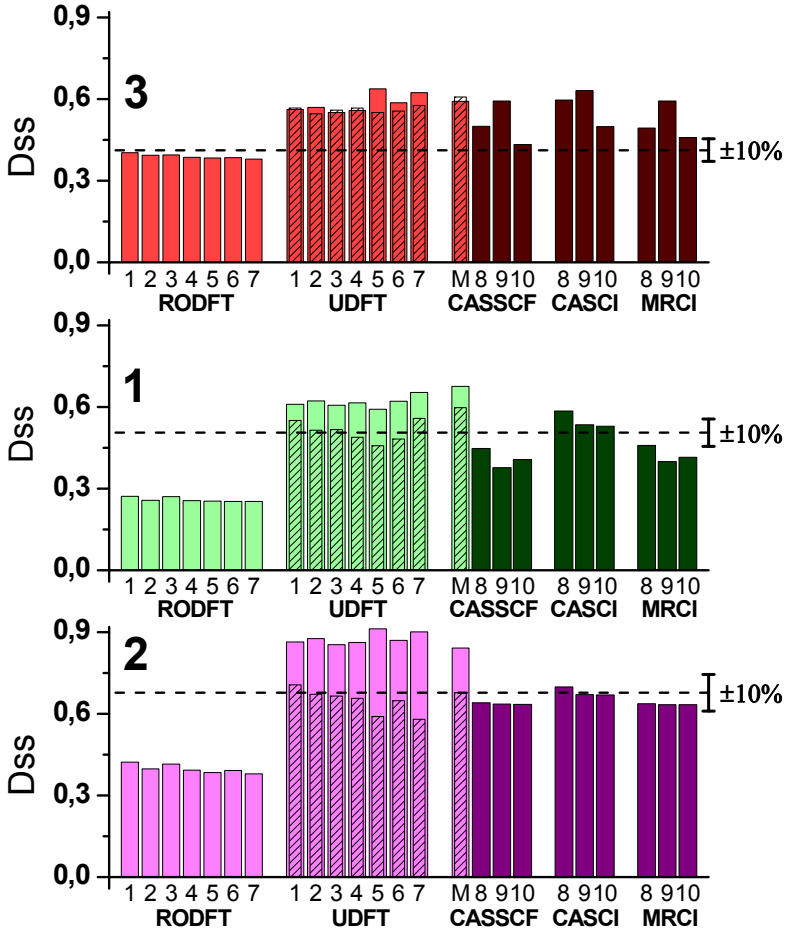

Figure S2. Calculated parameters D_{SS} of carbenes **1**, **2**, and **3** by DFT and *ab initio* methods. Calculations by McWeeny-Mizuno formalism are light-coloured, by *ab initio* formalism – dense-coloured. Contributions of the one-center spin-spin interactions are shown with shading. 1-7 – basis sets DZ, DZP, TZV, TZVP, TZVPP, EPRII, and EPRIII, respectively. 8 – 10 - reference wave functions T1, T1S1, and T1S2, respectively. M - calculated by McWeeny-Mizuno approach using the spin density matrices obtained from CASSCF(T1) wave functions. Dash lines show the experimental values of *D* from ref. [**Error! Bookmark not defined.**d] for carbene **2,** from ref. [**Error! Bookmark not defined.**] for carbene **3**, and from this work for carbene **1**.