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Skeletal isomerism within a 1,3-disilabicyclo[1.1.0]butane and 2,3-disilabuta-1,3-diene derivatives

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Contents

1. Experimental Details

1.1 General Procedures

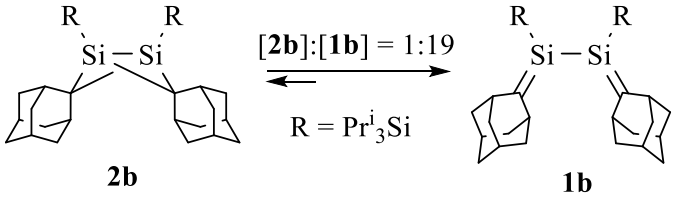
All reactions treating air-sensitive compounds were carried out under argon atmosphere using a high-vacuum line and standard Schlenk techniques, or a glove box, as well as dry and oxygen-free solvents. ^{1}H (500 MHz), ^{13}C (126 MHz) and ^{29}Si (99 MHz) NMR spectra were recorded on a Bruker Ascend 500 FT NMR spectrometer. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual ^{1}H and ^{13}C of the solvents; benzene-d_6 (^{1}H δ 7.16 and ^{13}C δ 128.0).[S1] ^{29}Si NMR chemical shifts were relative to Me_4Si in ppm. Sampling of **2b** was carried out using a VAC NEXUS 100027 type glove box. Mass spectra were recorded on a JEOL JMS-Q1050 spectrometer or a Bruker Daltonics SolariX 9.4T spectrometer. UV-vis spectra were recorded on a JASCO V-660. X-ray analysis were carried out using a Bruker APEXII CCD diffractometer. Melting points were recorded on a SRS OptiMelt MPA100 without correction.

1.2 Materials

Benzene-d_6 and hexane were dried in a tube covered with potassium mirror, and then distilled prior to use by using a vacuum line.

1',3'-Bis(triisopropylsilyl)-1',3'-disiladispiro[adamantane-2,2'-bicyclo[1.1.0]butane-4',2''-adamantane] **2b** was prepared according to the procedure described in the literature.[S2]

1.3 Thermal reaction of 2b



2b **1b**

A benzene-d_6 solution (0.5 mж) of **2b** (~5 mg) was heated in a sealed NMR tube at 60 °C for 8 h to provide a mixture of **2b** and 1,1,1,4,4,4-Hexaisopropyl-2,3-(diadamantan-2-ylidene)tetrasilane **1b** with the ratio of ~1:19 (NMR yields ~5% and ~95%). Upon further heating, the ratio of **2b**/**1b** was unchanged. Analytically pure **1b** was obtained by recrystallization from hexane at –35 °C.

1b: pale-yellow crystals; mp 164 – 165 °C; ^{1}H NMR (500 MHz, C_6D_6, 300 K) 1.28 (d, J = 6.5 Hz, 36H, CH_3), 1.35 (sept, J = 6.5 Hz, 6H, CH), 1.86 (brs, $\nu_{1/2}$ = 10.2 Hz, 4H, adamantylidene unit) 1.99-2.11 (m, 20H, adamantylidene unit), 3.26 (brs, $\nu_{1/2}$ = 11.7 Hz, 2H, adamantylidene

unit), 3.81 (brs, $\nu_{1/2}$ = 11.7 Hz, 2H, adamantylidene unit); $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 300 K) 14.3 (CH), 20.6 (CH_3), 29.4 (CH, adamantylidene unit), 38.2 (CH_2, adamantylidene unit), 41.2 (CH_2, adamantylidene unit), 41.8 (CH_2, adamantylidene unit), 42.0 (CH_2, adamantylidene unit), 42.3 (CH, adamantylidene unit), 42.7 (CH_2, adamantylidene unit), 43.2 (CH, adamantylidene unit), 196.1 (Si=C); $^{29}Si\{^{1}H\}$ NMR (99.4 MHz, C_6D_6, 300 K) 13.3 (*i*-Pr_3Si), 41.3 (Si=C); MS (EI, 70 eV) m/z (%) 638 (40, M^+), 595 (4, $M^+ - i$-Pr), 552 (4, $M^+ - i$-Pr×2) 481 (100, $M^+ - i$-Pr_3Si); Anal. calcd for $C_{38}H_{70}Si_4$: C, 71.39; H, 11.04%. Found: C,71.67; H, 11.19%; UV-vis (hexane, 300 K) λ_{max}/nm ($\varepsilon \times 10^{-3}$) 368 (2.9), 324 (33).

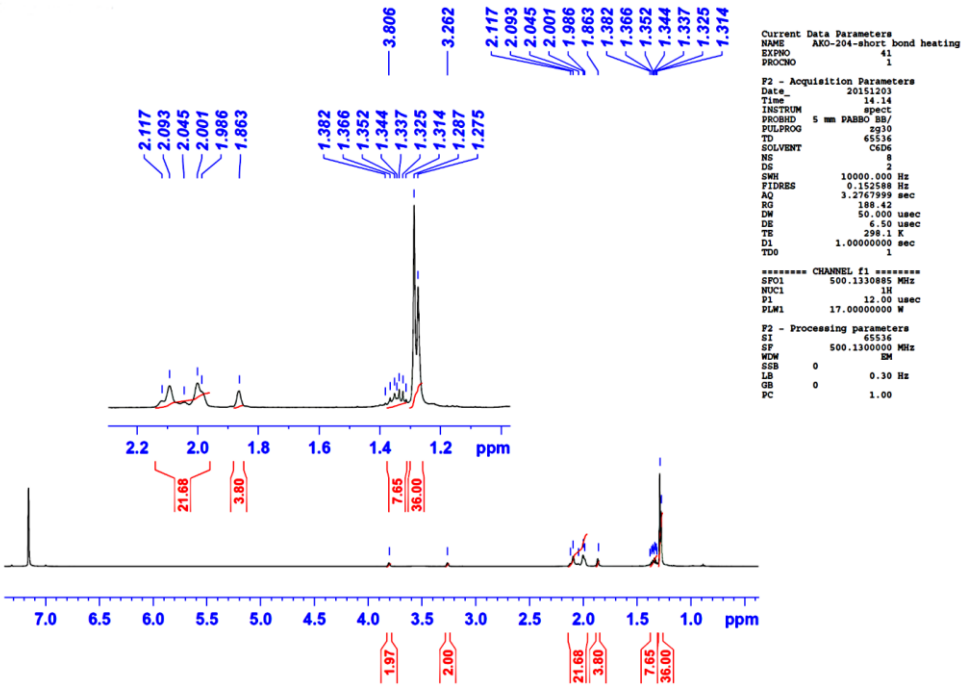


Figure S1. ^{1}H NMR spectrum of **1b** in C_6D_6 at 300 K (500 MHz).

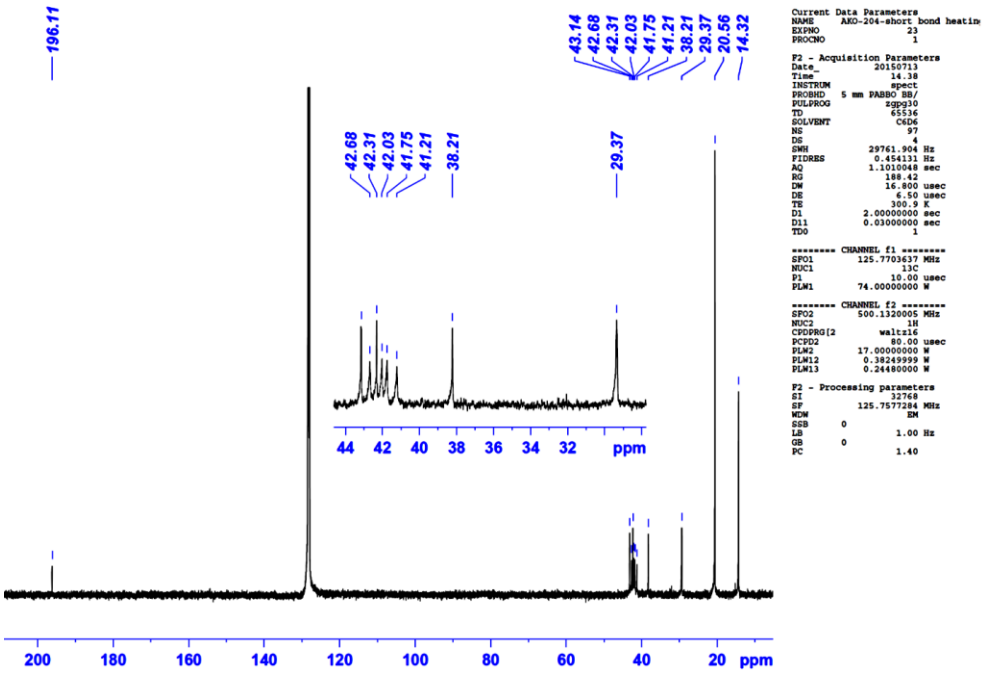


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **1b** in C_6D_6 at 300 K (126 MHz).

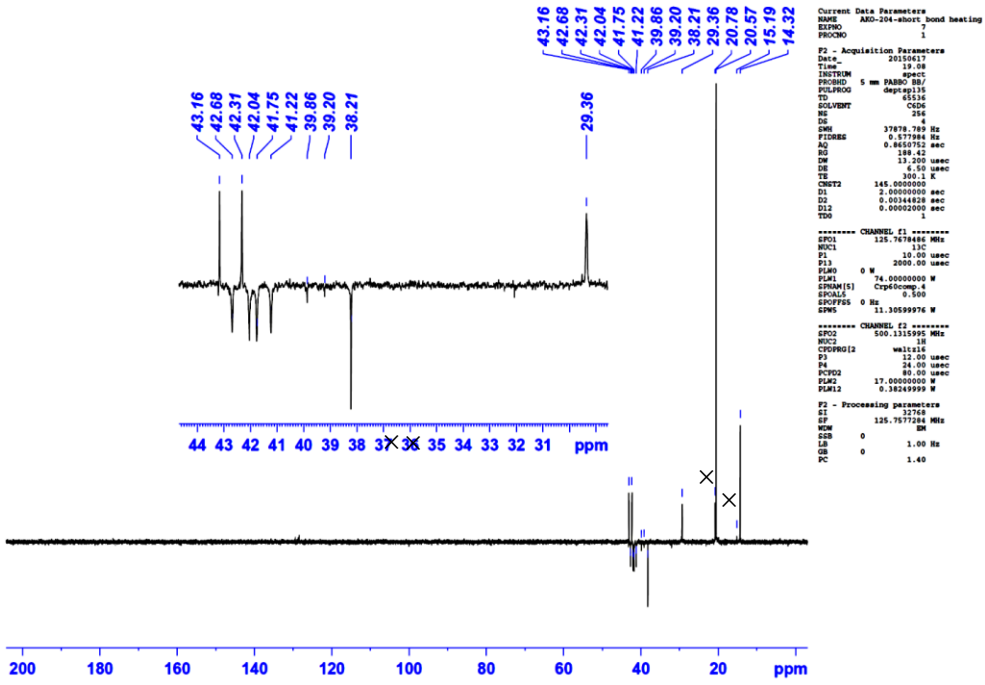


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **1b** in C_6D_6 at 300 K (126 MHz, DEPT 135, × = disilabicyclo[1.1.0]butane **2b**).

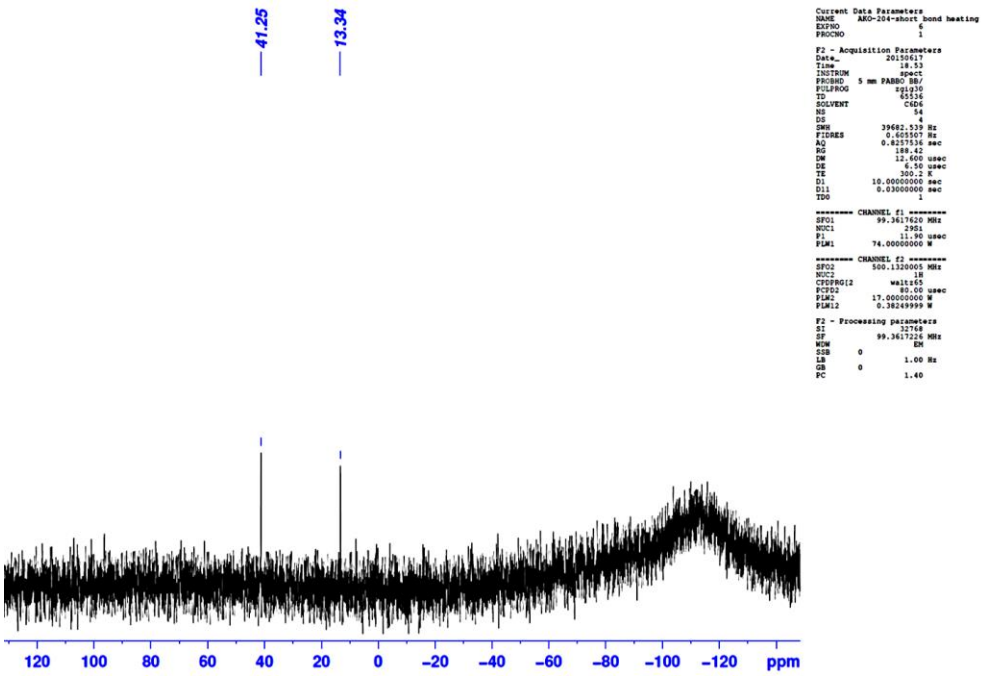


Figure S4. $^{29}Si\{^{1}H\}$ NMR spectrum of **1b** in C_6D_6 at 300 K (99.4 MHz).

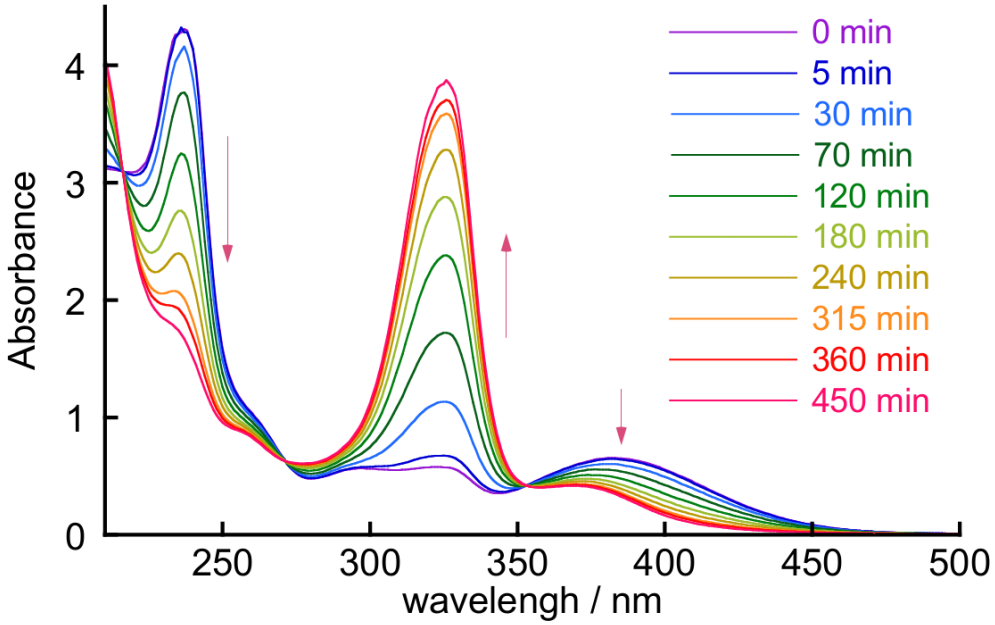


Figure S5. Time course of UV-vis absorption spectrum during isomerization of **2b** to **1b** in hexane at 65 °C.

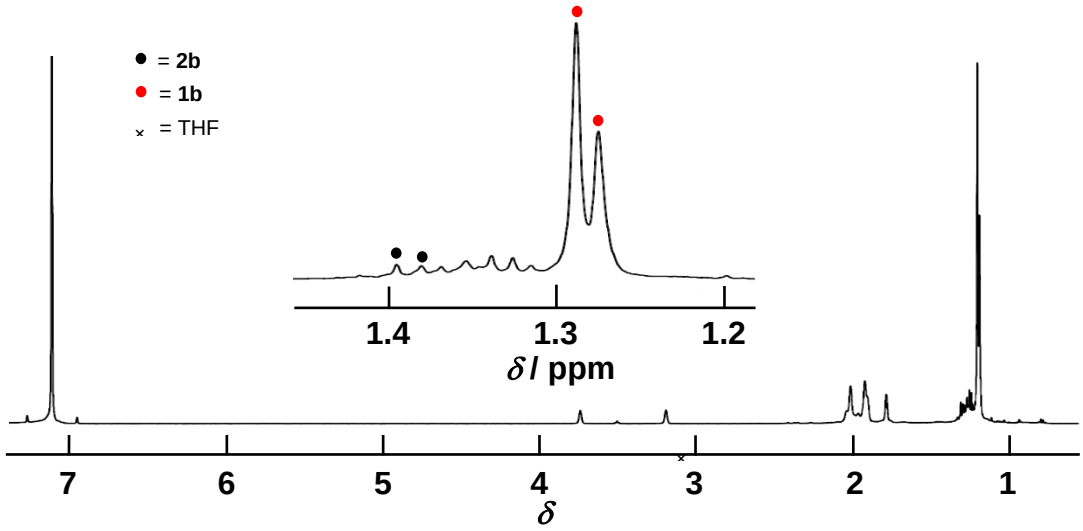


Figure S6. ^{1}H NMR spectrum of a benzene-d_6 solution of **2b** after heating at 60 °C for 8 hours.

2. Theoretical Calculations

All theoretical calculations were performed by using a Gaussian 09[S3] and GRRM14.[S4] The geometry of **1b** were optimized at the B3LYP-D3/6-311G(d) level of theory. The geometry of **2b** was reported in the previous paper.[S2] The supplemental file 'optimized_structures.xyz' contains the calculated Cartesian coordinates and energies of **1b** and **2b**.[S2] The transition energies and oscillator strengths of the electron transition in hexane (Table S2) were calculated using a time-dependent hybrid DFT method (TD-DFT) at the B3LYP-D3/def2-TZVP (hexane) level of theory and the calculated band position of **1b** was shown in Figure S7.

Table S2. Energies of **1b** and **2b**

Cpd	*E*/a.u.[b]	*E*+ZPVE/a.u.[b]	*E*(333.15K)/a.u.[b]	note (job name)
1b	-2648.763351499134 (0.0)	-2647.746585790206 (0.0)	-2647.844104929618 (0.0)	ti560MIN59
2b[a]	-2648.757900776529 (+14.3)	-2647.739928721033 (+17.5)	-2647.834801658061 (+24.4)	ti560MIN32, ti560MIN32f

[a] Ref. S2. [b]Relative energy in kJ mol^{-1} in the parentheses.

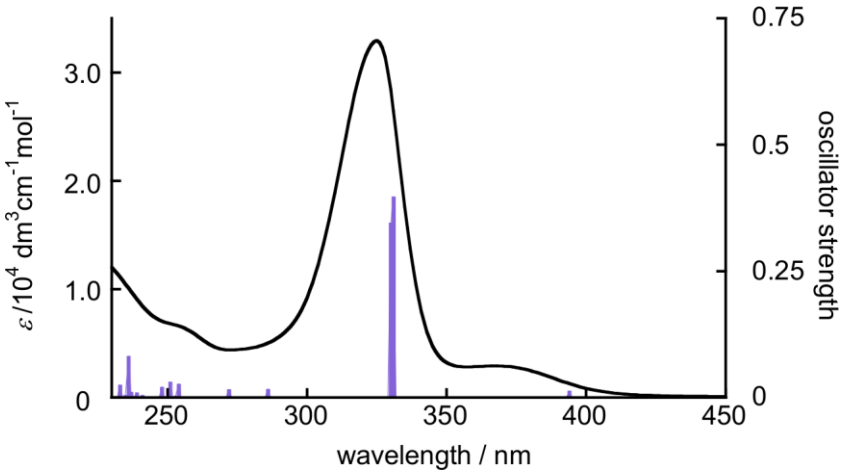


Figure S7. UV-vis spectra of **1b** in hexane at room temperature and theoretical band positions and oscillator strengths (vertical bars) calculated at the B3LYP-D3/def2-TZVP (hexane)//B3LYP-D3/6-311G(d) level of theory.

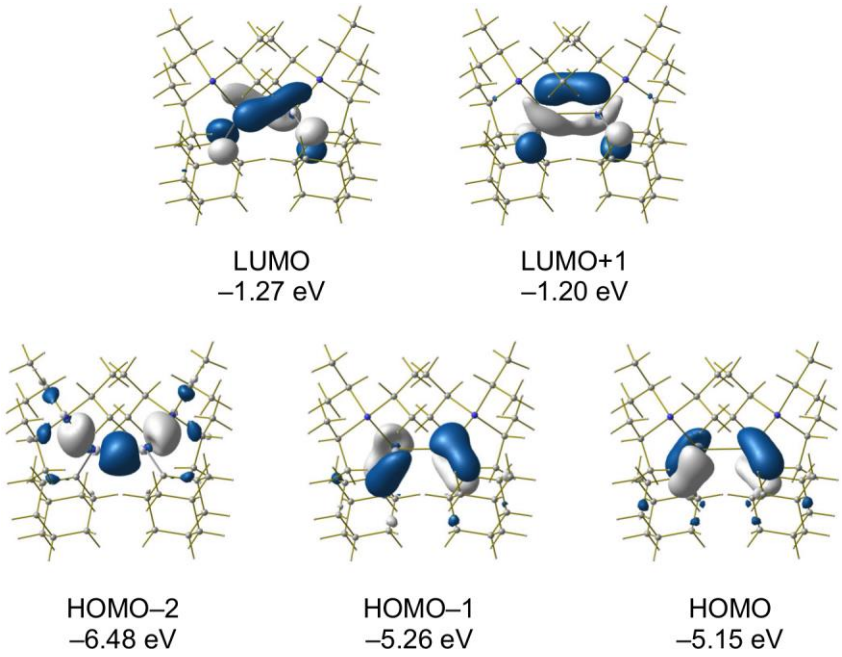


Figure S8. Frontier Kohn–Sham orbitals and their energy levels (in eV) of **1b** calculated at the B3LYP-D3/6-311G(d) level of theory. Isosurface level = 0.05 e^-/a.u.[S3]

Table S2. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of 1a Calculated at the TD-B3LYP-D3/def2-TZVP[hexane] Level of Theory (The 177th orbital is Highest Occupied Orbital Shown in Figure S8, JOB:ti560MIN59TD3)

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Excited State  1:     Singlet-A     3.1453 eV  394.18 nm  f=0.0001  <S**2>=0.000
    176 -> 178     -0.45762
    177 -> 179      0.53674

Excited State  2:     Singlet-B     3.1485 eV  393.79 nm  f=0.0131  <S**2>=0.000
    176 -> 179     -0.45403
    177 -> 178      0.53948

Excited State  3:     Singlet-B     3.7415 eV  331.37 nm  f=0.3973  <S**2>=0.000
    175 -> 178      0.10899
    176 -> 179      0.53072
    177 -> 178      0.44412

Excited State  4:     Singlet-A     3.7610 eV  329.66 nm  f=0.3453  <S**2>=0.000
    176 -> 178      0.52972
    177 -> 179      0.45176

Excited State  5:     Singlet-B     4.3306 eV  286.30 nm  f=0.0165  <S**2>=0.000
    175 -> 178      0.69163

Excited State  6:     Singlet-A     4.3639 eV  284.11 nm  f=0.0002  <S**2>=0.000
    175 -> 179      0.69551

Excited State  7:     Singlet-B     4.5605 eV  271.86 nm  f=0.0159  <S**2>=0.000
    177 -> 180      0.68324

Excited State  8:     Singlet-A     4.6554 eV  266.32 nm  f=0.0017  <S**2>=0.000
    176 -> 180      0.67232

Excited State  9:     Singlet-A     4.8788 eV  254.13 nm  f=0.0265  <S**2>=0.000
    169 -> 179     -0.12776
    173 -> 179      0.23419
    174 -> 178      0.51571
    176 -> 182      0.13720
    177 -> 181      0.31423
    177 -> 183     -0.11921

Excited State  10:     Singlet-B     4.9049 eV  252.77 nm  f=0.0036  <S**2>=0.000
    169 -> 178     -0.17714
    173 -> 178      0.32729
    174 -> 179      0.51358
    176 -> 181      0.17905
    177 -> 182      0.16957

Excited State  11:     Singlet-A     4.9349 eV  251.24 nm  f=0.0312  <S**2>=0.000
    173 -> 179     -0.10744
    174 -> 178     -0.31427
    176 -> 180     -0.14260
    176 -> 182      0.14027
    177 -> 181      0.57587

Excited State  12:     Singlet-B     5.0009 eV  247.92 nm  f=0.0207  <S**2>=0.000
    173 -> 178     -0.11867
    174 -> 179     -0.19077
    176 -> 181      0.53231
    176 -> 183     -0.14427
    177 -> 180     -0.11453
    177 -> 182      0.34461

Excited State  13:     Singlet-A     5.0869 eV  243.73 nm  f=0.0009  <S**2>=0.000
    176 -> 180      0.10815
    176 -> 182     -0.12329
    177 -> 181      0.16495
    177 -> 183      0.60611
    177 -> 184     -0.22242

Excited State  14:     Singlet-B     5.1494 eV  240.78 nm  f=0.0048  <S**2>=0.000
    176 -> 181     -0.40527
    176 -> 183     -0.26976
    176 -> 184      0.15407
    177 -> 182      0.43846
    177 -> 185     -0.10400
    177 -> 186     -0.13852

Excited State  15:     Singlet-B     5.1876 eV  239.00 nm  f=0.0098  <S**2>=0.000
    169 -> 178     -0.11135
    173 -> 178      0.55837
    174 -> 179     -0.38758

Excited State  16:     Singlet-A     5.2369 eV  236.75 nm  f=0.0106  <S**2>=0.000
    171 -> 178     -0.23845
    173 -> 179      0.53829
    174 -> 178     -0.23681
    176 -> 182      0.25358

Excited State  17:     Singlet-B     5.2443 eV  236.42 nm  f=0.0751  <S**2>=0.000
    172 -> 178      0.12712
    176 -> 183      0.54555
    176 -> 184     -0.15121
    177 -> 182      0.33743

Excited State  18:     Singlet-A     5.2537 eV  236.00 nm  f=0.0069  <S**2>=0.000
    170 -> 178     -0.12665
    173 -> 179     -0.27007
    176 -> 182      0.55736
    177 -> 181     -0.12189
    177 -> 183      0.20314

Excited State  19:     Singlet-A     5.2758 eV  235.01 nm  f=0.0044  <S**2>=0.000
    169 -> 179      0.32054
    170 -> 178      0.46694
    171 -> 178     -0.32805
    174 -> 178      0.20812

Excited State  20:     Singlet-B     5.2775 eV  234.93 nm  f=0.0005  <S**2>=0.000
    169 -> 178      0.46768
    170 -> 179      0.34072
    171 -> 179     -0.29760
    172 -> 178      0.14118
    173 -> 178      0.17500
    174 -> 179      0.13842

Excited State  21:     Singlet-B     5.3151 eV  233.27 nm  f=0.0239  <S**2>=0.000
    170 -> 179     -0.34141
    171 -> 179     -0.23134
    172 -> 178      0.54275
    176 -> 183     -0.11799

Excited State  22:     Singlet-A     5.3311 eV  232.57 nm  f=0.0011  <S**2>=0.000
    169 -> 179     -0.12032
    170 -> 178     -0.27938
    171 -> 178     -0.42015
    172 -> 179      0.42146
    173 -> 179     -0.16773

Excited State  23:     Singlet-B     5.4343 eV  228.15 nm  f=0.0154  <S**2>=0.000
    169 -> 178     -0.45491
    170 -> 179      0.46476
    171 -> 179     -0.17080
    172 -> 178      0.16015
    173 -> 178     -0.10163

Excited State  24:     Singlet-A     5.4405 eV  227.89 nm  f=0.0002  <S**2>=0.000
    176 -> 182     -0.11905
    177 -> 183      0.20488
    177 -> 184      0.64007

Excited State  25:     Singlet-A     5.4556 eV  227.26 nm  f=0.0000  <S**2>=0.000
    169 -> 179      0.49458
    170 -> 178     -0.41268
    171 -> 178     -0.10819
    172 -> 179     -0.23437

Excited State  26:     Singlet-B     5.4781 eV  226.33 nm  f=0.0123  <S**2>=0.000
    170 -> 179      0.17164
    171 -> 179      0.55660
    172 -> 178      0.36582

Excited State  27:     Singlet-A     5.4787 eV  226.30 nm  f=0.0009  <S**2>=0.000
    169 -> 179      0.30424
    171 -> 178      0.36352
    172 -> 179      0.49307
    173 -> 179      0.13387

Excited State  28:     Singlet-B     5.5037 eV  225.27 nm  f=0.0095  <S**2>=0.000
    176 -> 183     -0.15561
    176 -> 184     -0.16785
    177 -> 182      0.13431
    177 -> 185      0.54449
    177 -> 186      0.28469
    177 -> 188      0.11127

Excited State  29:     Singlet-B     5.5166 eV  224.75 nm  f=0.0031  <S**2>=0.000
    176 -> 183      0.16294
    176 -> 184      0.51811
    177 -> 185      0.35081
    177 -> 186     -0.25877

Excited State  30:     Singlet-A     5.5564 eV  223.14 nm  f=0.0000  <S**2>=0.000
    167 -> 179      0.41009
    168 -> 178      0.55628

Excited State  31:     Singlet-B     5.5588 eV  223.04 nm  f=0.0009  <S**2>=0.000
    167 -> 178      0.54710
    168 -> 179      0.42340

Excited State  32:     Singlet-B     5.5717 eV  222.53 nm  f=0.0133  <S**2>=0.000
    176 -> 184      0.31737
    177 -> 185     -0.11583
    177 -> 186      0.50158
    177 -> 188     -0.32415

Excited State  33:     Singlet-A     5.6020 eV  221.32 nm  f=0.0000  <S**2>=0.000
    176 -> 182      0.12569
    176 -> 185      0.59745
    176 -> 186      0.26695
    177 -> 187     -0.10385

Excited State  34:     Singlet-A     5.6749 eV  218.48 nm  f=0.0037  <S**2>=0.000
    176 -> 185     -0.23299
    176 -> 186      0.55046
    176 -> 188     -0.23646
    177 -> 187      0.21481

Excited State  35:     Singlet-A     5.7261 eV  216.53 nm  f=0.0024  <S**2>=0.000
    176 -> 185      0.15562
    176 -> 186     -0.13892
    176 -> 188      0.11693
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    176 -> 190      -0.12234
    177 -> 187       0.63651

Excited State  36:      Singlet-B     5.7355 eV  216.17 nm  f=0.0055  <S**2>=0.000
    176 -> 184       0.21079
    177 -> 185      -0.16290
    177 -> 186       0.20655
    177 -> 188       0.59300

Excited State  37:      Singlet-B     5.8057 eV  213.55 nm  f=0.0233  <S**2>=0.000
    176 -> 187       0.64320
    177 -> 190      -0.20703

Excited State  38:      Singlet-A     5.8248 eV  212.86 nm  f=0.0000  <S**2>=0.000
    176 -> 185      -0.18506
    176 -> 186       0.16060
    176 -> 188       0.60436
    177 -> 184       0.10066
    177 -> 189       0.16937

Excited State  39:      Singlet-B     5.8720 eV  211.14 nm  f=0.0244  <S**2>=0.000
    165 -> 178       0.14149
    166 -> 179       0.15094
    167 -> 178      -0.39779
    168 -> 179       0.50940
    175 -> 180       0.16893

Excited State  40:      Singlet-A     5.8733 eV  211.10 nm  f=0.0057  <S**2>=0.000
    165 -> 179      -0.14632
    166 -> 178      -0.38208
    167 -> 179       0.43973
    168 -> 178      -0.34271

Excited State  41:      Singlet-A     5.9056 eV  209.94 nm  f=0.0000  <S**2>=0.000
    165 -> 179       0.22013
    166 -> 178       0.49828
    167 -> 179       0.34981
    168 -> 178      -0.23960

Excited State  42:      Singlet-B     5.9251 eV  209.25 nm  f=0.1598  <S**2>=0.000
    165 -> 178       0.34357
    166 -> 179       0.34015
    167 -> 178       0.16267
    168 -> 179      -0.21545
    175 -> 180       0.38577

Excited State  43:      Singlet-A     5.9445 eV  208.57 nm  f=0.0000  <S**2>=0.000
    164 -> 178      -0.22742
    176 -> 186      -0.19829
    176 -> 188      -0.14887
    176 -> 190       0.12837
    176 -> 192       0.10944
    177 -> 189       0.54836
    177 -> 194      -0.12601

Excited State  44:      Singlet-B     5.9472 eV  208.47 nm  f=0.2385  <S**2>=0.000
    164 -> 179       0.14137
    165 -> 178      -0.35441
    166 -> 179      -0.27569
    175 -> 180       0.45688
    176 -> 187      -0.10842

Excited State  45:      Singlet-B     5.9638 eV  207.89 nm  f=0.0072  <S**2>=0.000
    164 -> 179      -0.18579
    176 -> 187       0.10477
    176 -> 189       0.32192
    176 -> 191      -0.12788
    176 -> 194      -0.14995
    177 -> 186      -0.13384
    177 -> 190       0.48484
    177 -> 192       0.10608

Excited State  46:      Singlet-A     5.9900 eV  206.98 nm  f=0.0071  <S**2>=0.000
    163 -> 179      -0.11917
    164 -> 178       0.59430
    165 -> 179      -0.20661
    177 -> 189       0.23909

Excited State  47:      Singlet-B     6.0069 eV  206.40 nm  f=0.0250  <S**2>=0.000
    163 -> 178      -0.11226
    164 -> 179       0.33038
    165 -> 178      -0.13424
    166 -> 179       0.22330
    176 -> 187       0.15011
    176 -> 189      -0.20790
    177 -> 190       0.36717
    177 -> 192      -0.28278

Excited State  48:      Singlet-A     6.0396 eV  205.29 nm  f=0.0163  <S**2>=0.000
    166 -> 178      -0.12888
    176 -> 190      -0.21876
    176 -> 192       0.10823
    177 -> 189       0.18018
    177 -> 191       0.58778
    177 -> 193       0.10587

Excited State  49:      Singlet-B     6.0482 eV  204.99 nm  f=0.0715  <S**2>=0.000
    164 -> 179       0.26718
    165 -> 178      -0.26987
    166 -> 179       0.28347
    175 -> 180      -0.15111
    176 -> 189       0.31682
    176 -> 191       0.12549
    177 -> 192       0.28435

Excited State  50:      Singlet-A     6.1005 eV  203.23 nm  f=0.0007  <S**2>=0.000
    176 -> 190       0.59492
    177 -> 187       0.10098
    177 -> 191       0.27920

Excited State  51:      Singlet-B     6.1074 eV  203.01 nm  f=0.0044  <S**2>=0.000
    164 -> 179       0.41953
    165 -> 178       0.35152
    166 -> 179      -0.36500
    176 -> 191       0.17207
    177 -> 192       0.10470

Excited State  52:      Singlet-A     6.1121 eV  202.85 nm  f=0.0005  <S**2>=0.000
    164 -> 178       0.22182
    165 -> 179       0.60279
    166 -> 178      -0.26336

Excited State  53:      Singlet-B     6.1426 eV  201.84 nm  f=0.0611  <S**2>=0.000
    164 -> 179      -0.16584
    176 -> 189      -0.29259
    176 -> 191       0.44257
    177 -> 190       0.19337
    177 -> 192       0.33871

Excited State  54:      Singlet-B     6.1776 eV  200.70 nm  f=0.0274  <S**2>=0.000
    164 -> 179      -0.10471
    176 -> 189       0.30382
    176 -> 191       0.42935
    176 -> 193       0.15806
    177 -> 192      -0.38216

Excited State  55:      Singlet-A     6.1935 eV  200.18 nm  f=0.0200  <S**2>=0.000
    176 -> 192      -0.42947
    177 -> 189       0.19976
    177 -> 193       0.12467
    177 -> 194       0.46141

Excited State  56:      Singlet-A     6.2195 eV  199.35 nm  f=0.0002  <S**2>=0.000
    176 -> 192      -0.32417
    177 -> 193       0.43244
    177 -> 194      -0.39340
    177 -> 196      -0.10112

Excited State  57:      Singlet-A     6.2808 eV  197.40 nm  f=0.0031  <S**2>=0.000
    175 -> 181       0.61829
    175 -> 183      -0.14075
    177 -> 193      -0.24162

Excited State  58:      Singlet-B     6.2822 eV  197.36 nm  f=0.0032  <S**2>=0.000
    176 -> 189       0.15120
    176 -> 193      -0.23619
    176 -> 194       0.43830
    177 -> 195      -0.29880
    177 -> 197      -0.26199
    177 -> 200       0.12636

Excited State  59:      Singlet-A     6.2962 eV  196.92 nm  f=0.0017  <S**2>=0.000
    175 -> 181       0.27610
    176 -> 190       0.16088
    176 -> 192       0.34575
    177 -> 193       0.43682
    177 -> 194       0.19872

Excited State  60:      Singlet-B     6.3372 eV  195.65 nm  f=0.0065  <S**2>=0.000
    163 -> 178       0.55952
    164 -> 179       0.11976
    176 -> 193       0.21947
    176 -> 194       0.19334
    177 -> 195       0.17895

Excited State  61:      Singlet-B     6.3653 eV  194.78 nm  f=0.1310  <S**2>=0.000
    163 -> 178      -0.35052
    176 -> 191      -0.11973
    176 -> 193       0.37209
    176 -> 194       0.35402
    177 -> 195       0.18763

Excited State  62:      Singlet-A     6.3861 eV  194.15 nm  f=0.0045  <S**2>=0.000
    175 -> 181       0.10317
    175 -> 183       0.38812
    175 -> 184      -0.10087
    176 -> 190      -0.10105
    176 -> 195       0.23418
    176 -> 197       0.33169
    176 -> 200      -0.20923
    177 -> 196      -0.21025

Excited State  63:      Singlet-B     6.3869 eV  194.12 nm  f=0.3083  <S**2>=0.000
    175 -> 180       0.14203
    175 -> 182      -0.16697
    176 -> 193      -0.36065
    176 -> 194       0.18621
    176 -> 196      -0.10503
    177 -> 195       0.12033
    177 -> 197       0.41373
    177 -> 200      -0.16325

Excited State  64:      Singlet-A     6.4058 eV  193.55 nm  f=0.0000  <S**2>=0.000
    163 -> 179      -0.21654
    176 -> 192      -0.10890
    176 -> 195       0.20841
    176 -> 202      -0.12581
    177 -> 196       0.56245
    177 -> 201      -0.14199
```

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4. optimized_structure.xyz

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