Electronic Supplementary Information

A theoretical analysis of the structure and properties of $B_{26}H_{30}$ isomers. Consequences to the laser and semiconductor doping capabilities of large borane clusters

Jan Macháček[a], Antonio Francés-Monerris*[b], Naiwrit Karmodak[c], Daniel Roca-Sanjuán[d], Jindřich Fanfrlík[e], Michael G. S. Londesborough[a], Drahommír Hnyk*[a] and Eluvathingal D. Jemmis[c]*

[a]*Institute of Inorganic Chemistry, Czech Academy of Sciences, CZ-250 68 Husinec-Řež, Czech Republic*

**Email: hnyk@iic.cas.cz*

[b]*Université de Lorraine, CNRS, LPCT, F54000 Nancy, France*

**Email: antonio.frances@univ-lorraine.fr*

[c]*Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 56001, India*

**Email: jemmis@gmail.com*

[d]*Instituto de Ciencia Molecular, Universitat de València, P.O. Box 22085, 46071 València, Spain*

[e]*Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, CZ -166 10 Praha 6, Czech Republic*

Details on multiconfigurational calculations

The lowest-lying singlet excited state of the three isomers was optimized using the complete-active-space self-consistent field (CASSCF) method[1] as implemented in the MOLCAS 8 software package.[2] Given the relatively large size of the $B_{26}H_{30}$ systems, the small 6-31G basis set have been used in order to make the CASSCF optimizations affordable. An active space of eight electrons distributed into the most relevant four occupied and four virtual molecular orbitals (MOs), hereafter CASSCF(8,8), have been used to conduct the minimizations, and two states have been demanded in the state-average (SA)-CASSCF procedure. The S_0/S_1 conical intersection (CI) structures have been optimized by means of the restricted Lagrange multipliers technique in which the lowest-energy point is obtained under the restriction of energy degeneracy between the two considered states.[3] A large number of optimization steps (>100) were needed to converge the CI geometries given the large geometrical distortions needed to reach energy degeneracy.

An active space composed of 12 electrons distributed into 12 MOs, hereafter CASSCF(12,12) (see Figures S1-S3), in combination with the much larger double-ξ atomic natural orbital of ANO-S type with the contraction scheme C,N,O[3s2p1d]/H[2s1p] (hereafter, ANO-S-VDZP), has been employed to compute the final energies reported in the present work. Four states have been demanded in the SA-CASSCF procedure. To include the necessary dynamic electronic correlation, complete-active-space second-order perturbation theory (CASPT2)[4,5] computations have been performed on top of the SA-CASSCF wave functions maintaining all core electrons frozen during the perturbation step. The recommended value of 0.25 au for the ionization-potential electron-affinity (IPEA) parameter has been used throughout given its good description of related boron hydride compounds.[6–10] An imaginary level shift of 0.2 au has been used in order to minimize the effect of weakly intruder states. The small S_0/S_1energy differences (≤0.35 eV) at the CASPT2/ANO-S-VDZP level confirms the CI nature of the minimum-energy crossing points calculated with the SA-CASSCF/6-31G method.

The potential energy surfaces (PESs) linking the S_0 minima with the corresponding S_1 equilibrium geometries and S_0/S_1 CI points have been constructed by means of the linear interpolation of internal coordinates (LIIC) technique, which yields a connected, yet not optimized, chemical pathway. Therefore, the energy profiles should be considered as upper bounds.

No symmetry constraints have been imposed in any multiconfigurational calculation performed in this work. All multiconfigurational calculations have been conducted with the MOLCAS 8 suite of programs.[2]

Table S1: The relative stability of the different isomers of $B_{26}H_{30}$

isomers	Relative Energy (kcal/mol)
anti-transoid-E-*anti*-transoid	0.0
anti-transoid-E-*syn*-transoid	1.06
syn-transoid-E-*syn*-transoid	2.48
anti-transoid-Z-*syn*-transoid	8.75
anti-transoid-Z-*anti*-transoid	8.97
syn-transoid-Z-*syn*-transoid	10.14
anti-transoid-E-*anti*-cisoid	50.82
anti-transoid-Z-*anti*-cisoid	51.32
anti-cisoid-E-*syn*-transoid	52.15
anti-cisoid-Z-*syn*-transoid	53.45
anti-transoid-E-syn-cisoid	54.97
syn-transoid-E-*syn*-cisoid	56.35
anti-transoid-Z-*anti*-cisoid	57.36
anti-cisoid-E-*anti*-cisoid	100.01
anti-cisoid-Z-*syn*-cisoid	100.37
anti-cisoid-E-*syn*-cisoid	106.35
anti-cisoid-Z-*anti*-cisoid	107.74
syn-cisoid-E-*syn*-cisoid	113.94
syn-transoid-Z-*syn*-cisoid	117.21
syn-cisoid-Z-*syn*-cisoid	no minima

Table S2. CASPT2 relative energies of the S_0 and S_1 states at the Franck-Condon (FC), S_1 equilibrium geometry and CI structure for the three $B_{26}H_{30}$ isomers. Oscillator strengths are shown within parenthesis)

State	FC	S_1 min	CI
	3a		
S_0	0.00	0.71	5.59
S_1	3.52 (0.498)	3.34	5.77
	3b		
S_0	0.00	0.69	5.85
S_1	3.64 (0.562)	3.34	6.09
	3c		
S_0	0.00	0.36	7.16
S_1	3.82 (0.620)	3.29	7.51

Table S3. Magnitude of the electrostatic potential on the 0.001 a.u. molecular surface computed at the HF/cc-pVDZ level in kcal mol^{-1}.

Molecule	V_{max}	V_{min}
3a	32.8	-8.9
3b	34.5	-9.2
3c	33.7	-9.1
anti-$B_{18}H_{22}$	32.5	-8.2
syn-$B_{18}H_{22}$	34.1	-8.9

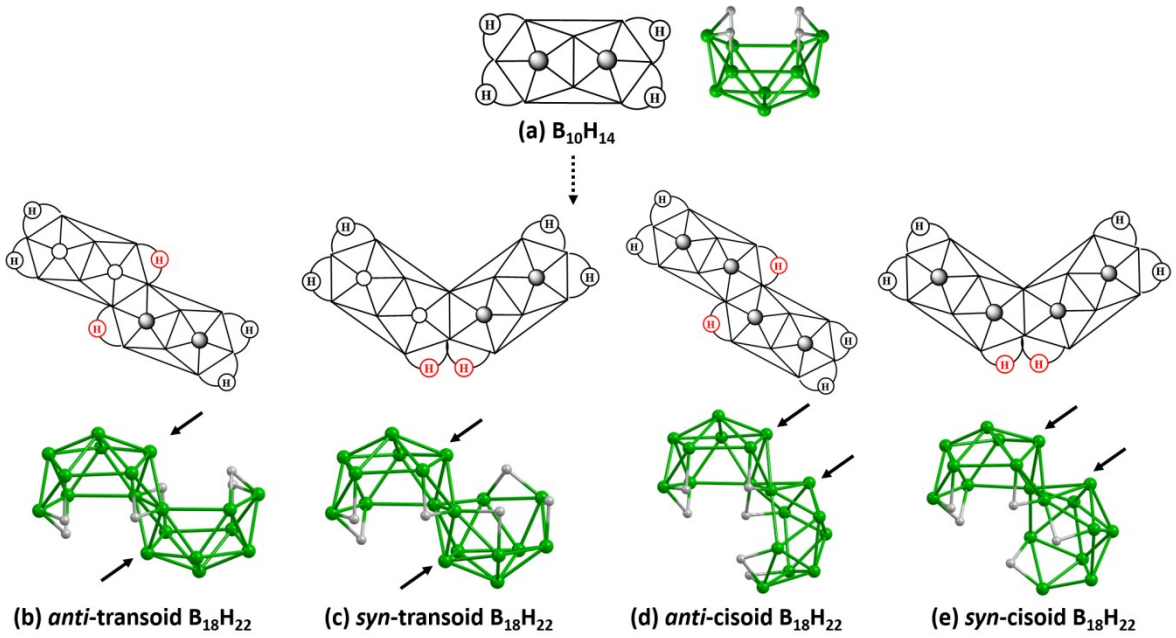

Figure S1: The aerial and 3D structural models for $B_{18}H_{22}$ isomers. The orientation of the BH "caps" (black arrows) around the shared positions gives the transoid and cisoid specifications, whereas the arrangement of open faces in decaborane units gives the *syn* and *anti*-nomenclature. The terminal H atoms are omitted. In the aerial models, bridging H atoms near the shared B-B bonds are shown in red, whereas the peripheral H bridges are shown in black. The B atoms at the center of pentagonal rings are denoted by filled or hollow circles. Filled circles denote vertices pointing above the pentagonal rings and hollow ones those pointing below the plane.

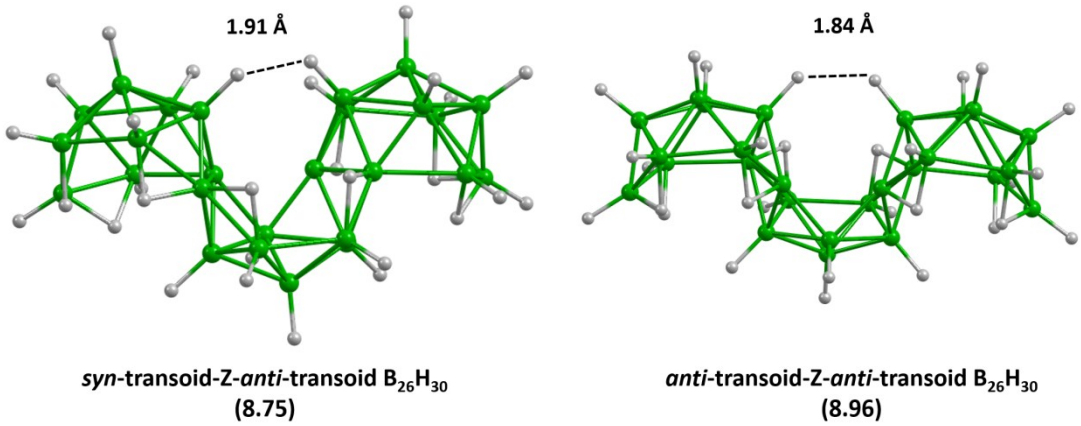

Figure S2. The optimized geometry for the two structural isomers of $B_{26}H_{30}$ with Z-type connection of the peripheral decaborane units to the central decaboranyl unit. The relative energies in kcal/mol are given within the parenthesis.

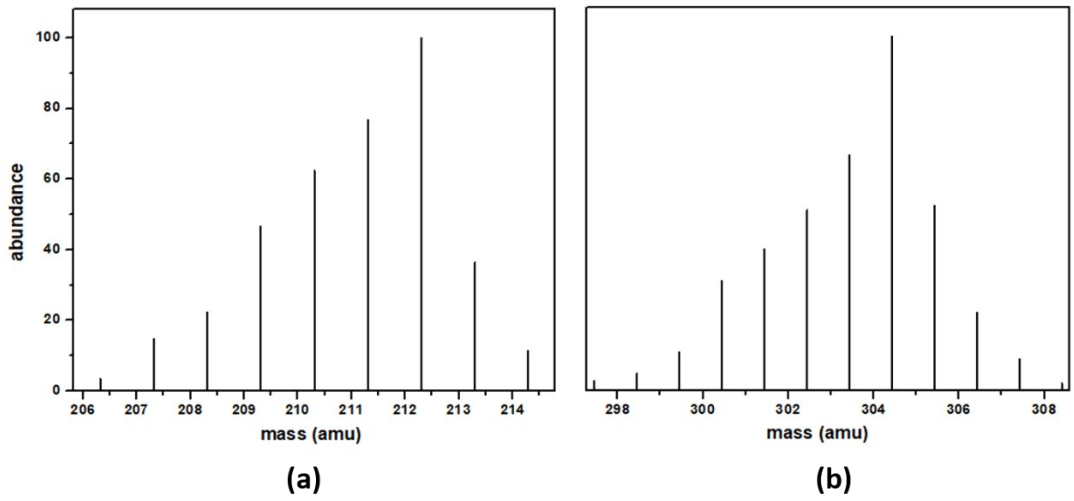

Figure S3: Simulated mass spectra for (a) *anti*-$B_{18}H_{22}$ and (b*)* **3a**.

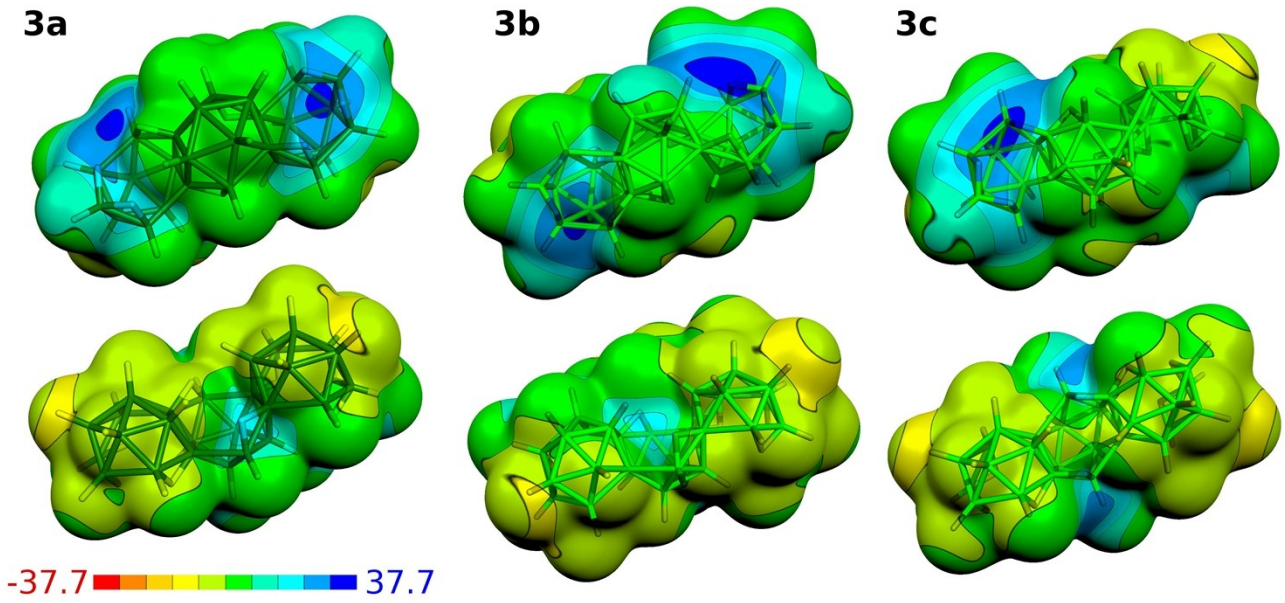
3a
3b
3c
-37.7
37.7

Figure S4. The electrostatic potential on the 0.001 a.u. molecular surface of **3a**, **3b** and **3c** computed at the HF/cc-pVDZ level. The color range is in kcal mol^{-1}.

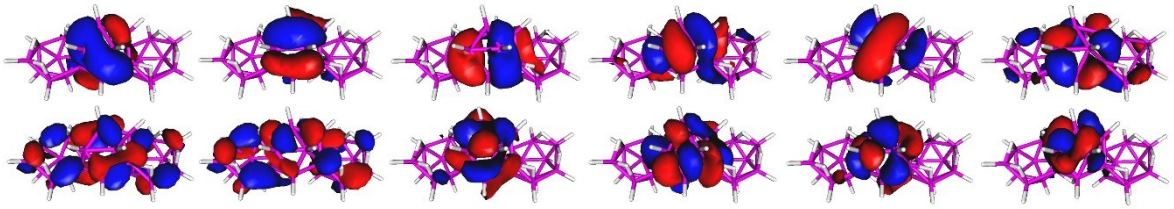

Figure S5. Natural CASSCF(12,12) orbitals for the **3a** molecule. The geometry corresponds to the S_0 equilibrium structure.

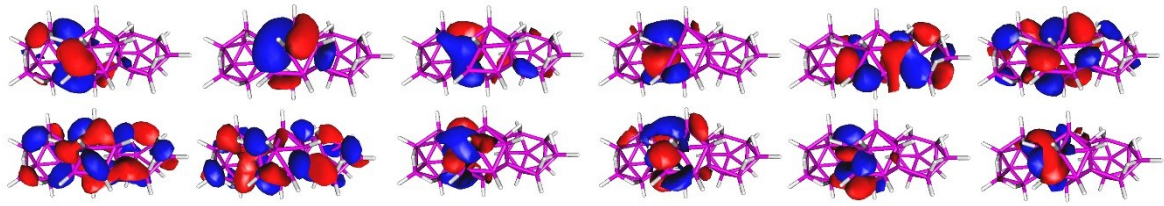

Figure S6. Natural CASSCF(12,12) orbitals for the **3b** molecule. The geometry corresponds to the S_0 equilibrium structure.

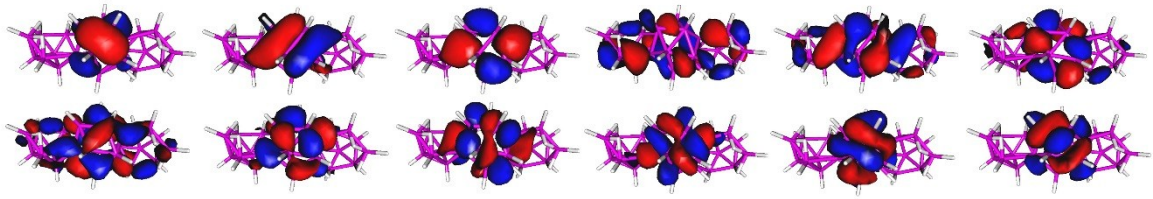

Figure S7. Natural CASSCF(12,12) orbitals for the **3c** molecule. The geometry corresponds to the S_0 equilibrium structure.

Simulated absorption and emission spectra

The absorption and emission spectra were obtained by using a semi-classical approach in which firstly the distribution of nuclear geometries around the ground (S_0) and excited (S_1) state equilibrium structures at 300 K was sampled by means of a Wigner distribution with 50 points using the Newton-X program[11] and the B3LYP/6-31G* and TD-B3LYP/6-31G* frequencies for S_0 and S_1, respectively, and secondly by convoluting the computed TD-B3LYP/6-311G* excitation energies and oscillator strengths in hexane at each geometry using Gaussian functions with a full-width at half-length of 0.3 eV.

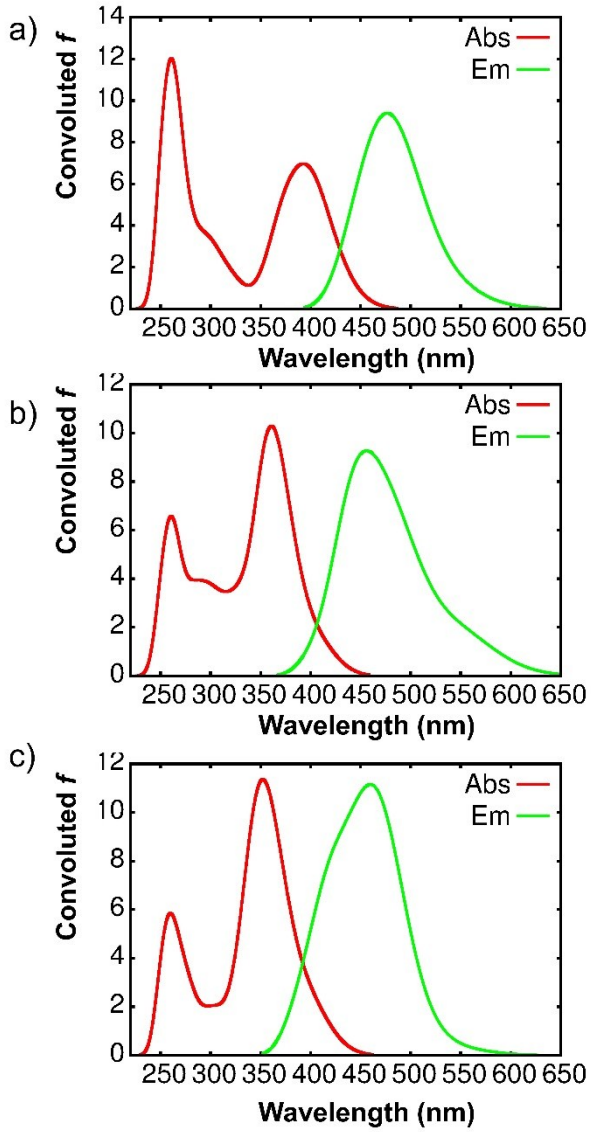

Figure S8. Absorption and emission spectra for a) **3a**, b) **3b**, and c) **3c** obtained with TD-DFT. The S_0 and S_1 regions of the PESs were sampled by means of a Wigner distribution at 300 K, obtaining sets of 50 different geometries. Spectra were obtained as a convolution of the excitation energies and oscillator strengths using Gaussian functions with a full-width at half-length of 0.3 eV.

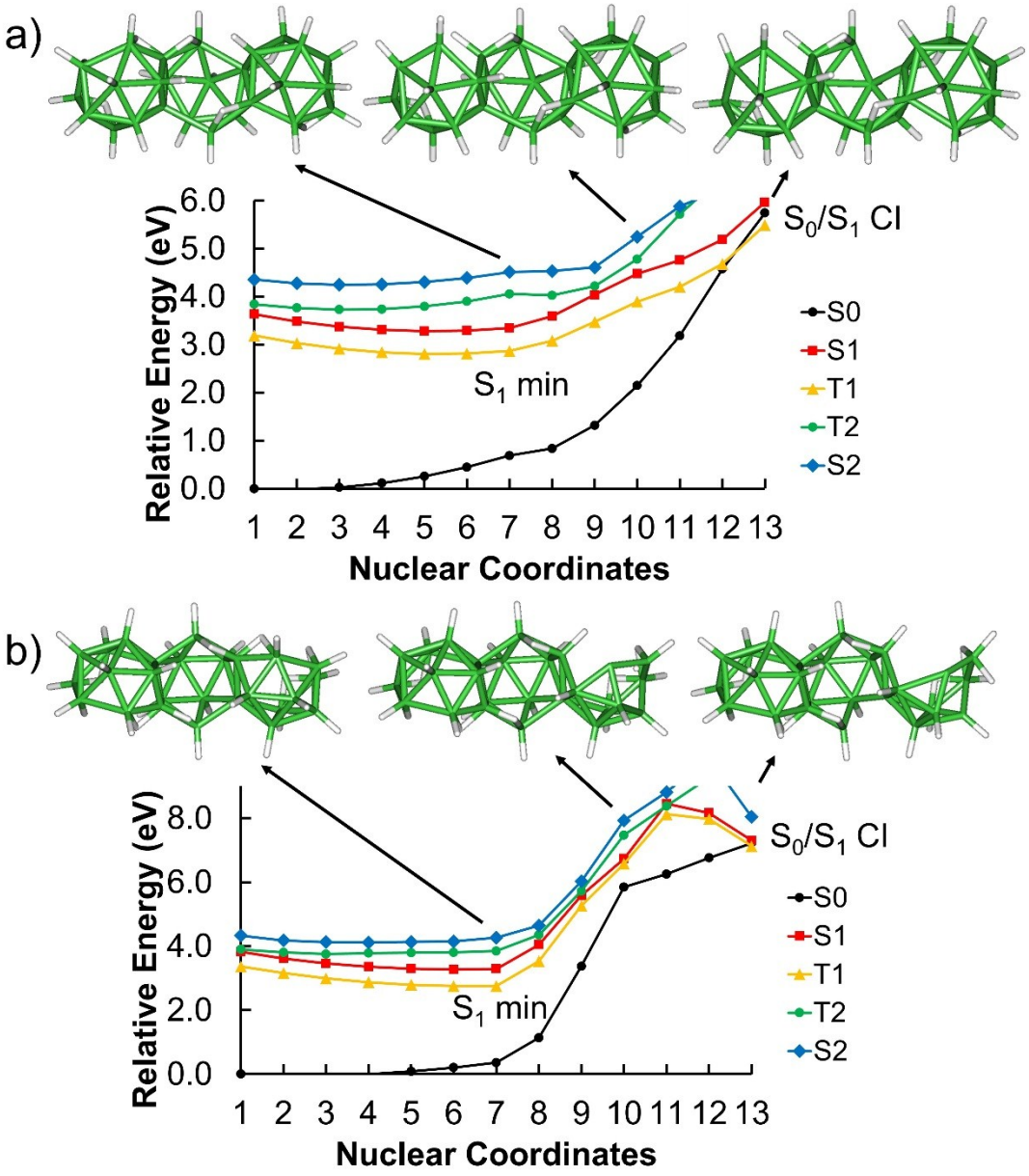

Figure S9. CASPT2 PESs for the non-radiative decay of a) **3b** and b) **3c**. The profiles were obtained by coordinate interpolations between the ground-state minima (nuclear coordinates = 1), S_1 equilibrium structures (nuclear coordinates = 7), and S_0/S_1 conical intersections (CI, nuclear coordinates = 13).

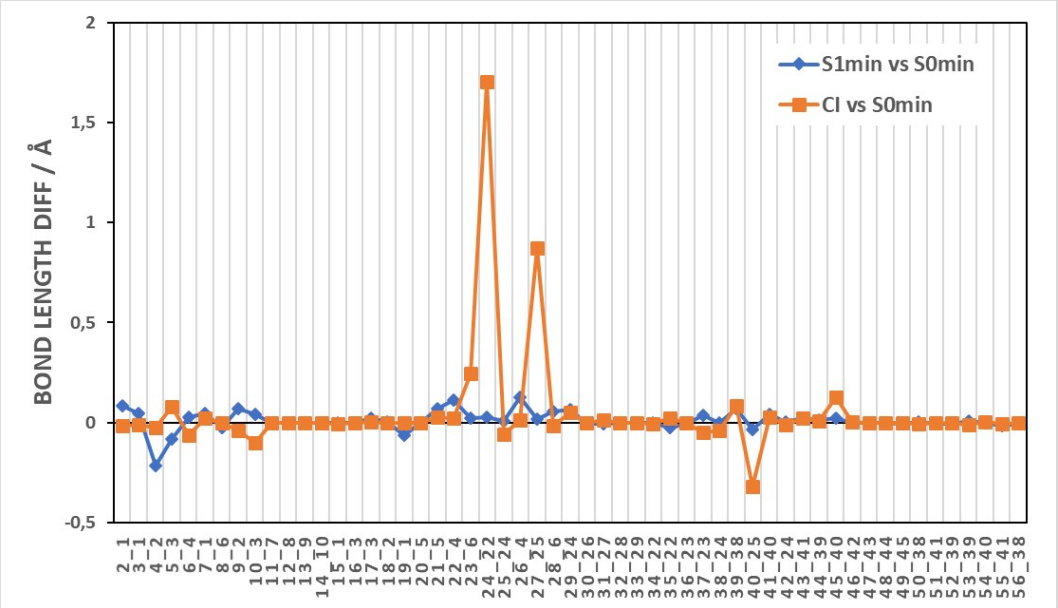

Figure S10. Bond length differences (in Å) between the excited-state (S_1 min) and ground-state or FC (S_0 min) equilibrium structure and between the CI and ground-state (S_0 min) equilibrium structure obtained for the CASSCF/CASPT2 determination of the photophysical radiationless decay mechanism for **3a**. Atom labelling is given in the Cartesian coordinates below.

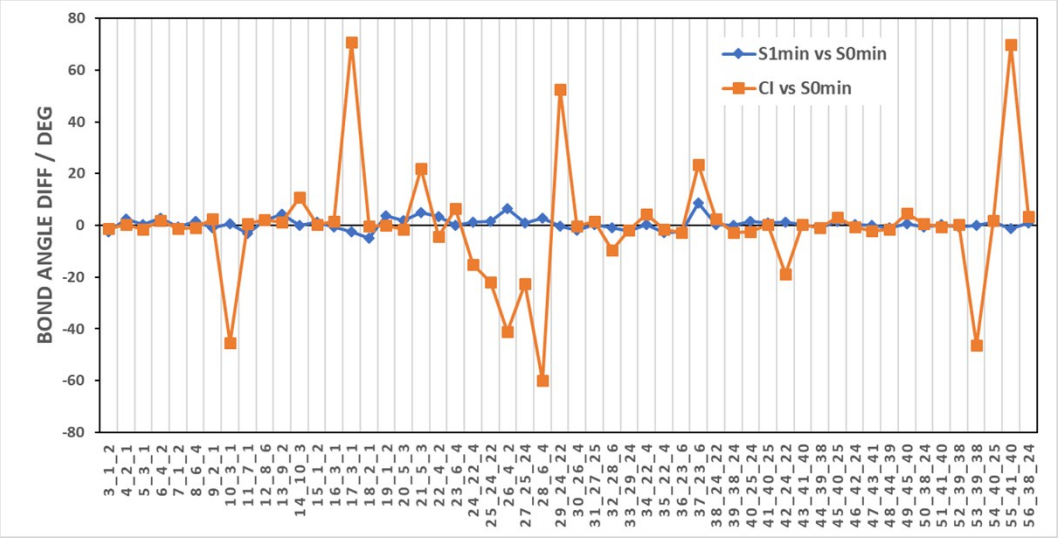

Figure S11. Bond angle differences (in degree) between the excited-state (S_1 min) and ground-state or FC (S_0 min) equilibrium structure and between the CI and ground-state (S_0 min) equilibrium structure obtained for the CASSCF/CASPT2 determination of the photophysical radiationless decay mechanism for **3a**. Atom labelling is given in the Cartesian coordinates below.

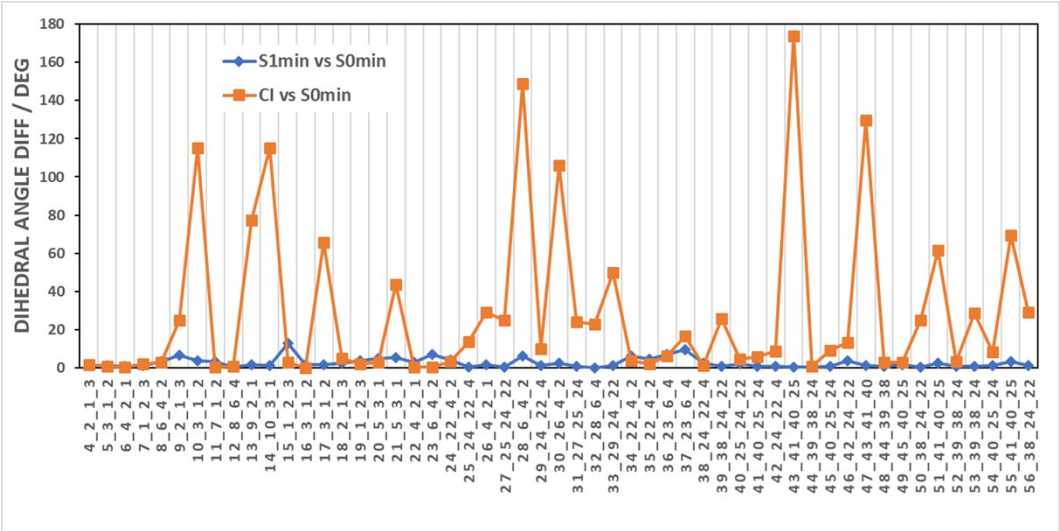

Figure S12. Dihedral angle differences (in degree) between the excited-state (S_1 min) and ground-state or FC (S_0 min) equilibrium structure and between the CI and ground-state (S_0 min) equilibrium structure obtained for the CASSCF/CASPT2 determination of the photophysical radiationless decay mechanism for **3a**. Atom labelling is given in the Cartesian coordinates below.

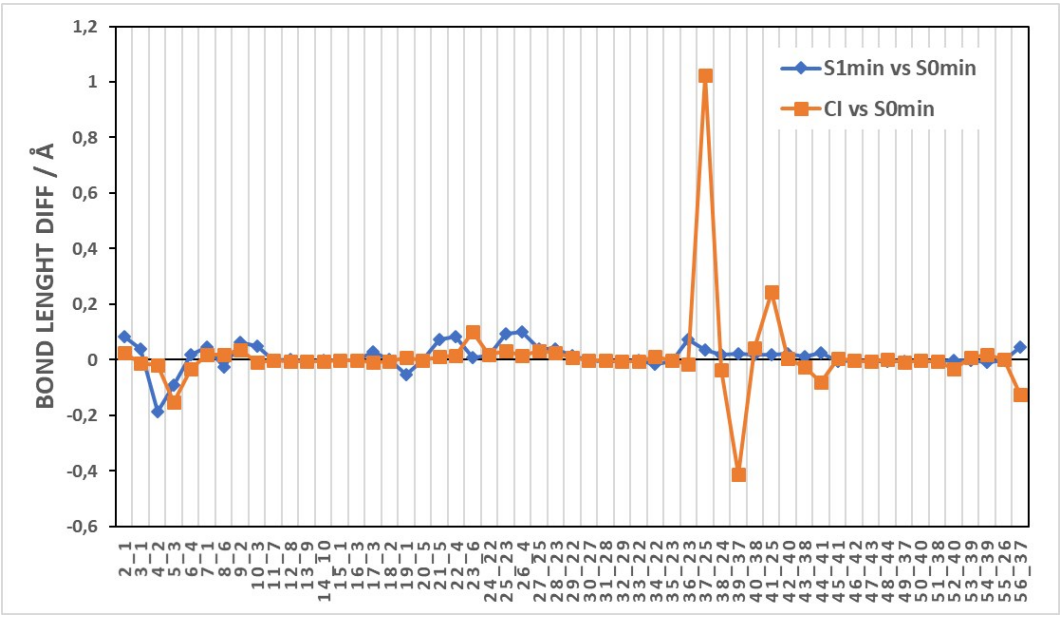

Figure S13. Bond length differences (in Å) between the excited-state (S_1 min) and ground-state or FC (S_0 min) equilibrium structure and between the CI and ground-state (S_0 min) equilibrium structure obtained for the CASSCF/CASPT2 determination of the photophysical radiationless decay mechanism for **3b**. Atom labelling is given in the Cartesian coordinates below.

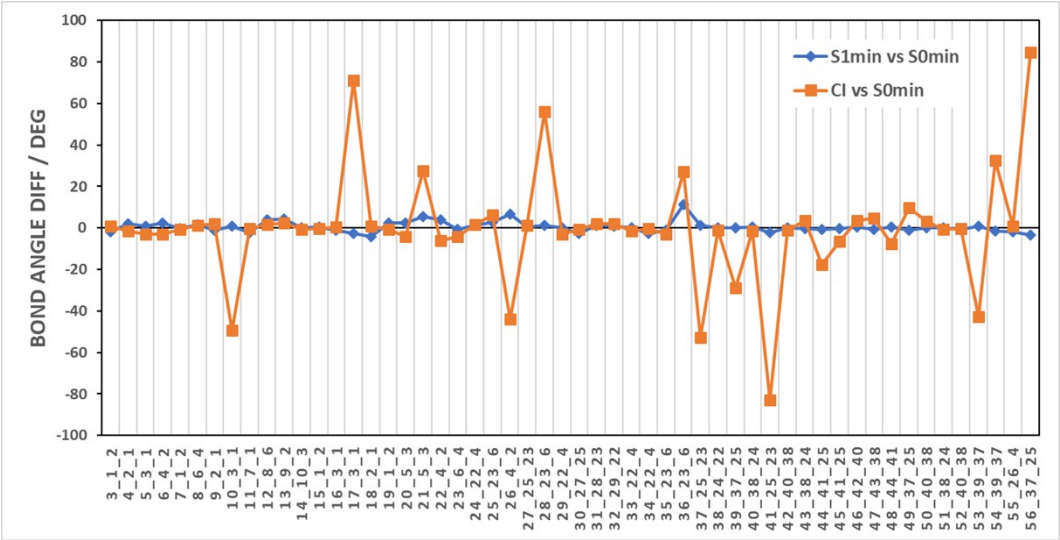

Figure S14. Bond angle differences (in degree) between the excited-state (S_1 min) and ground-state or FC (S_0 min) equilibrium structure and between the CI and ground-state (S_0 min) equilibrium structure obtained for the CASSCF/CASPT2 determination of the photophysical radiationless decay mechanism for **3b**. Atom labelling is given in the Cartesian coordinates below.

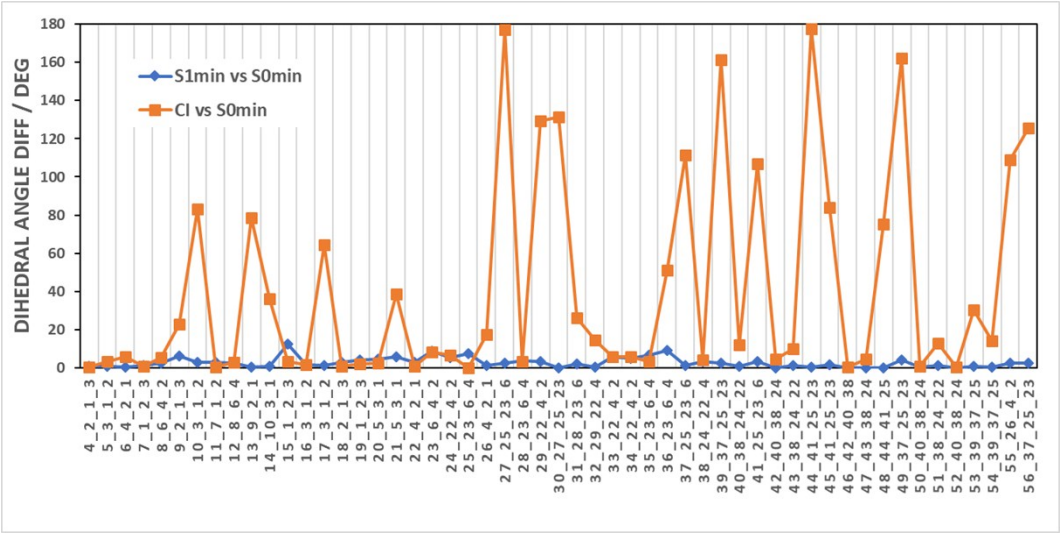

Figure S15. Dihedral angle differences (in degree) between the excited-state (S_1 min) and ground-state or FC (S_0 min) equilibrium structure and between the CI and ground-state (S_0 min) equilibrium structure obtained for the CASSCF/CASPT2 determination of the photophysical radiationless decay mechanism for **3b**. Atom labelling is given in the Cartesian coordinates below.

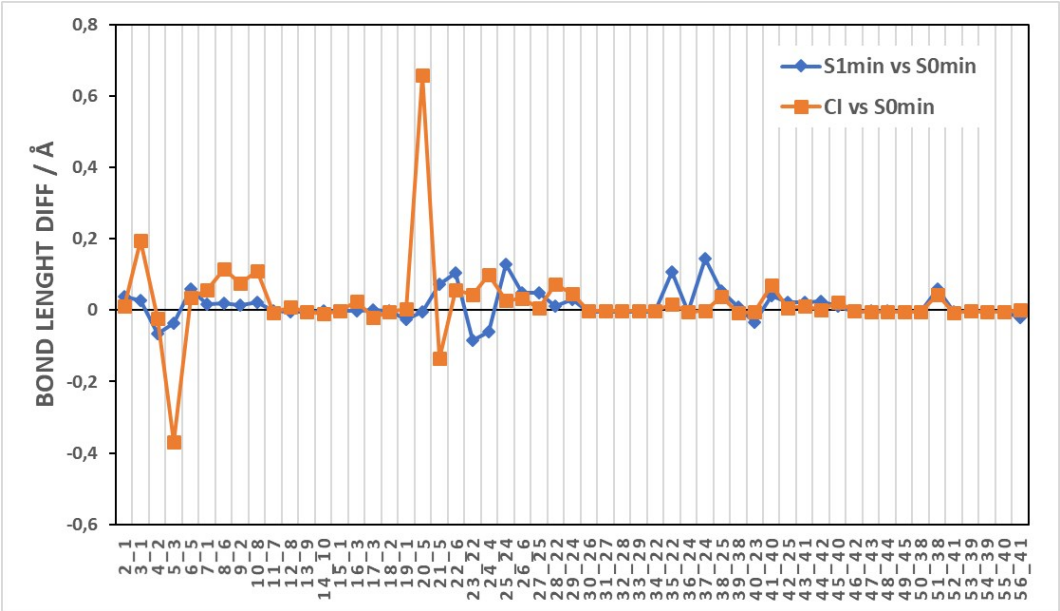

Figure S16. Bond length differences (in Å) between the excited-state (S_1 min) and ground-state or FC (S_0 min) equilibrium structure and between the CI and ground-state (S_0 min) equilibrium structure obtained for the CASSCF/CASPT2 determination of the photophysical radiationless decay mechanism for **3c**. Atom labelling is given in the Cartesian coordinates below.

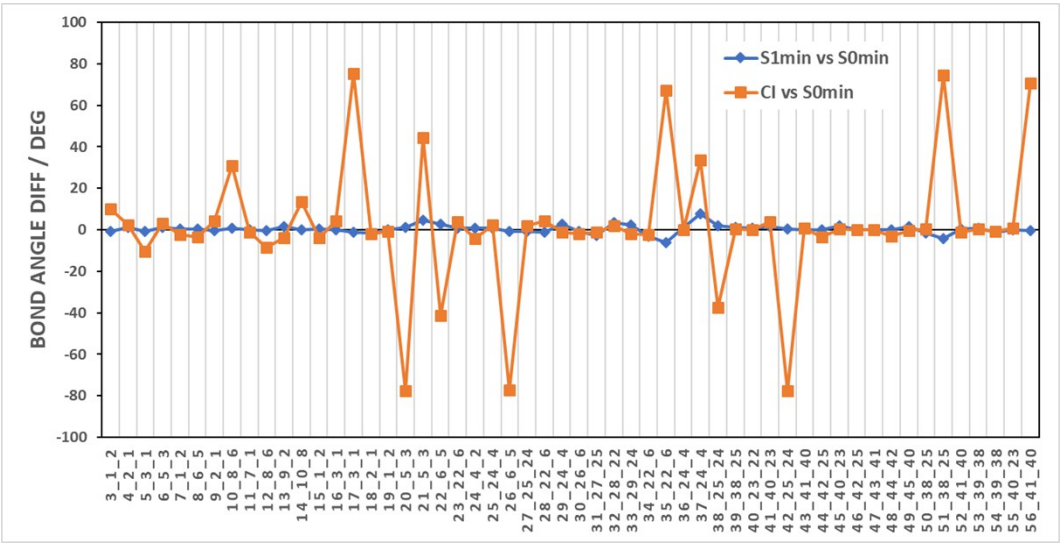

Figure S17. Bond angle differences (in degree) between the excited-state (S_1 min) and ground-state or FC (S_0 min) equilibrium structure and between the CI and ground-state (S_0 min) equilibrium structure obtained for the CASSCF/CASPT2 determination of the photophysical radiationless decay mechanism for **3c**. Atom labelling is given in the Cartesian coordinates below.

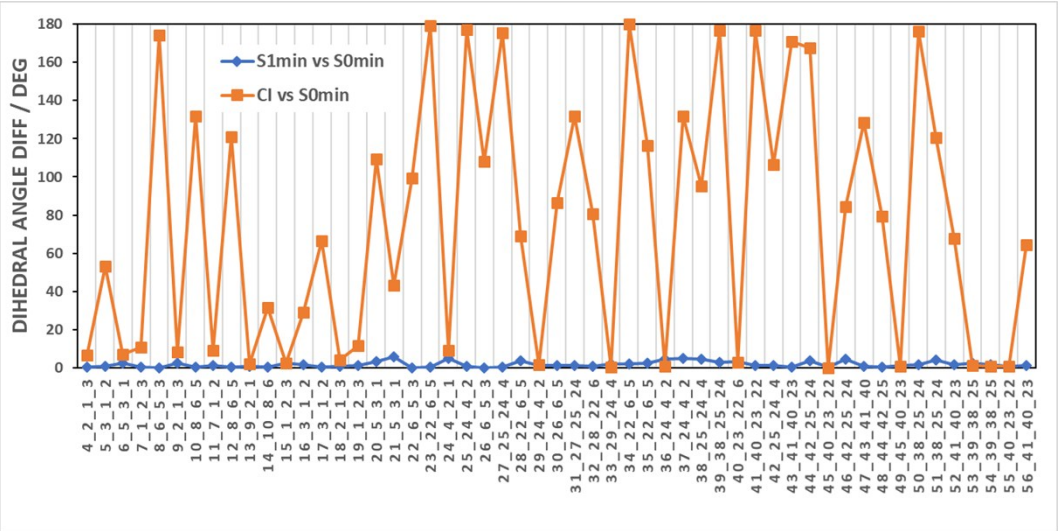

Figure S18. Dihedral angle differences (in degree) between the excited-state (S_1 min) and ground-state or FC (S_0 min) equilibrium structure and between the CI and ground-state (S_0 min) equilibrium structure obtained for the CASSCF/CASPT2 determination of the photophysical radiationless decay mechanism for **3c**. Atom labelling is given in the Cartesian coordinates below.

Cartesian coordinates of the studied structures

3a (S_0 min) – B3LYP

B1	-0.64046167836381429	4.7616303695287865	0.59139773138652185
B2	-1.6226997671969292	3.4664022069560225	-0.16286356547872705
B3	1.0175599999170994	4.5766704371828446	-0.12643617385438366
B4	-0.77337318497668261	1.6588945286732006	-9.7873513915728516E-002
B5	1.8486513094867709	2.8006873198235671	-0.15900729947400583
B6	0.88266963795933262	1.4409031202830029	0.61781021151530424
B7	-0.50705935441947403	4.4918163237850592	-1.1039242247042573
B8	0.72923357617511353	1.7644260682353894	-1.1103022989117608
B9	-0.72923282116541610	2.7410264339844304	-1.4836073149546185
B10	0.90890623245544067	3.4759774864596680	-1.4896278889554788
H11	-0.84469788277167568	5.3069154211820715	-1.8843274000107149
H12	1.0743208235010544	0.97134272831607515	-1.9079657877240233
H13	-1.3638862499673736	2.4313400091222275	-2.4292651406307870
H14	1.5556514997943840	3.7514294964218435	-2.4371264625017672
H15	-1.0408029998600064	5.7059237737936988	1.1690329220573930
H16	1.7355972401484314	5.5106909015752947	-9.4755057789050689 5E-002
H17	0.55082918573702544	4.4264288898871627	1.1069368102875825
H18	-2.8001173420261556	3.5102042986984507	-0.13933233620810592
H19	-1.2412191660324208	3.7003640898737209	1.0920822017083200
H20	3.0223889437887270	2.7124222793950534	-0.21044249524522940
H21	1.5041061468901529	2.5498515891514129	1.0835385858955053
B22	-1.7532654971719568	0.34269551766182654	0.69681944226545833

B23	1.7532686459658624	-0.34269390018797768	0.69682043128334026
B24	-0.88266801349037394	-1.4409022880233693	0.61781009818444865
B25	0.77337451945132318	-1.6588955072153724	-9.78737655601368273E-002
B26	-0.62592762026339577	1.3525919943522016	1.6301015044570668
B27	0.62593006395944328	-1.3525922585781363	1.6301012399275170
B28	0.82442552324029694	0.37212584026494638	2.0070333009289114
B29	-0.82442223815084004	-0.37212591911377829	2.0070338205811158
H30	-0.94990105973963734	2.1388726964968470	2.4445096754729554
H31	0.94990277069228901	-2.1388731543319031	2.4445095028405461
H32	1.4483790597803279	0.65992363970075907	2.9664060177829588
H33	-1.4483760241849024	-0.65992344163893923	2.9664064561528791
H34	-2.9286950567505841	0.40172314906908990	0.74454435902045435
H35	-1.4127662165168970	0.57920295595884652	-0.55145794509022772
H36	2.9286982379176041	-0.40172074629672155	0.74454547500516599
H37	1.4127690481744590	-0.57920239255444073	-0.55145666591247766
B38	-1.8486522780519452	-2.8006853054809970	-0.15900786282371016
B39	-1.0175625705347040	-4.5766692164502194	-0.12643885455509574
B40	1.6226995550751313	-3.4664039414184291	-0.16286291939895914
B41	0.64046048373807718	-4.7616308462193642	0.59139926075395299
B42	-0.72923329842899498	-1.7644254888859905	-1.1103024757849957
B43	0.50705812782046167	-4.4918176471467826	-1.1039228302165973
B44	-0.90890775661185008	-3.4759758908550955	-1.4896301823355256
B45	0.72923304812553857	-2.7410294668338069	-1.4836076799559588
H46	-1.0743208135255462	-0.97134211326470110	-1.9079658230646952
H47	0.84469585027078697	-5.3069174714977674	-1.8843255973670929
H48	-1.5556536178930644	-3.7514267173299887	-2.4371286888786239
H49	1.3638865926136401	-2.4313451508907384	-2.4292661165225713
H50	-1.5041075992116200	-2.5498497574467804	1.0835381961226873
H51	1.0408010876578626	-5.7059243465783238	1.1690347880848215
H52	-1.7356005687303251	-5.5106890554568775	-9.47566390948272330E-002
H53	-0.55083270238805171	-4.4264300007484767	1.1069347716958791
H54	2.8001170878512958	-3.5102067946807827	-0.13933126884338132
H55	1.2412189440051093	-3.7003647915090823	1.0920830475772427
H56	-3.0223898637684083	-2.7124199551986408	-0.21044357522452173

3a (S_1 min) – CASSCF

B1	-0.64394831495557048	4.8498738490038154	0.55390916235254051
B2	-1.5974621742131412	3.4056665016741041	-0.17078931876813125
B3	1.0612049160834705	4.6042944068349900	-0.15247239920765726
B4	-0.83063741929583912	1.8025196828492271	-4.06789535109902192E-002
B5	1.8557741657028022	2.9028853841065652	-7.25048638427170933E-002
B6	0.82900617251438957	1.5302254090431500	0.71747658695691952
B7	-0.47811707011924937	4.4671166653272412	-1.1631090794476335
B8	0.75252705397188646	1.7425877784589205	-1.0089549799755264
B9	-0.66436536810193625	2.7392488209652126	-1.5871736439845734
B10	0.96404672347791720	3.4502886462218938	-1.5242138341853468
H11	-0.80749039100969422	5.2777667988914008	-1.9518348546371447
H12	1.0558003583720919	0.89938631292202043	-1.7712198116658804
H13	-1.2278121876033554	2.3742287778388085	-2.5533853279218586

H14	1.6498694198113228	3.6812596831123430	-2.4526067887979011
H15	-1.0540152957240532	5.9086323093652133	0.86242680163292529
H16	1.7557835157619008	5.5534519753140286	-0.21383174532557642
H17	0.53010921831375668	4.5945909313432720	1.0892945572240078
H18	-2.7715911615872315	3.5181134473899478	-0.18183842204900208
H19	-1.2304837542139839	3.9180531922975690	1.1576425939288271
H20	3.0251026607912972	2.7763972916212083	-1.60694995249841058E-002
H21	1.4226147991408835	2.5584412715568243	1.1960478381688402
B22	-1.8154671684016255	0.33700215079757623	0.75023020472093971
B23	1.7365152416731406	-0.26080498073052033	0.64916706919091072
B24	-0.91232692095503565	-1.4575987228489882	0.60578698913275120
B25	0.75214366915211506	-1.6824059697204921	-0.11089515217192253
B26	-0.64559798193151541	1.3379083712461786	1.7800900502174979
B27	0.63268375447569114	-1.3999232667272064	1.6416509604976259
B28	0.82293594507702705	0.32366443512101056	2.0634330378455790
B29	-0.83284349506671895	-0.37762157766497834	2.0657164790875298
H30	-0.93337934718044824	2.0959885041796986	2.6273936615750655
H31	0.94001895407576874	-2.2039508199485582	2.4378718202717780
H32	1.4508041789860964	0.57913934502849440	3.0253064645211252
H33	-1.4241957263419893	-0.73908413567283449	3.0168506632720060
H34	-2.9859869803672869	0.36778877209753930	0.84690863471237121
H35	-1.4780662851720852	0.68979715650101336	-0.44263766978481706
H36	2.9079552202084131	-0.25255446089525319	0.60565070806904064
H37	1.3450540911346180	-0.65753786127100466	-0.58173457316429356
B38	-1.8805736956640233	-2.8250415584520843	-0.14731808449415235
B39	-0.99538258194257756	-4.6527751812580158	-0.15008431658568727
B40	1.6301436260691193	-3.4348137177038591	-0.18571964804061175
B41	0.67551798018235842	-4.8119409848975998	0.55596627872457405
B42	-0.77381679923572400	-1.7728309314116517	-1.1275255319181190
B43	0.52045126552416354	-4.5117167405873513	-1.1555124061732884
B44	-0.94895564734986559	-3.5117724273642179	-1.4998049865451759
B45	0.69384862507587430	-2.7662589913217572	-1.5345490766266403
H46	-1.0737331123742975	-0.96157231866722037	-1.9192589420538242
H47	0.86199930998907093	-5.3068887891783882	-1.9506328986025077
H48	-1.6110415216047718	-3.7981448872841086	-2.4289042256979845
H49	1.3041251569488963	-2.4268374293840838	-2.4796163331561956
H50	-1.4763088008791525	-2.5746158326326452	1.0795948781221718
H51	1.1015259700677320	-5.7682059745164960	1.0847650248634240
H52	-1.7069445375987324	-5.5862246666924804	-0.11782118925808022
H53	-0.50564635945098979	-4.5082650641714279	1.0833169415974653
H54	2.8043911531889743	-3.4761223587109265	-0.19206041347397601
H55	1.2779824342856774	-3.7719932902310069	1.0534349818963109
H56	-3.0537454817155512	-2.7888149311641075	-0.14137941799003012

3a (S_0/S_1 CI) – CASSCF

B1	-0.19057144519241753	5.0695081605632870	0.42010273007789339
B2	-1.3987652184847403	3.9477786525417558	-0.24175844652973741
B3	1.3664320958678737	4.4944059569625896	-0.28461355042241704
B4	-0.95484261573880203	2.0381107367984419	-1.06804598945478713E-002

B5	1.7897937763918952	2.5048921940303899	-0.13404790705009847
B6	0.53696897333823101	1.5048512998525201	0.73728870187361217
B7	-0.12632866833442469	4.5919253611941722	-1.2536253320090236
B8	0.43680629908453233	1.6629779000926501	-1.0160371405905824
B9	-0.60313127229114083	2.9634335327962629	-1.4837334158265265
B10	1.0200203620527133	3.2880797877755774	-1.5312723518111173
H11	-0.29193769677584297	5.3599613456094684	-2.1278339671350639
H12	0.56311133403376334	0.75579802770018045	-1.7483761848634831
H13	-1.2664501249505522	2.7254130279786786	-2.4261100484985461
H14	1.7070642488264576	3.3388431831051091	-2.4846121080273260
H15	-0.38655427148650262	6.1300952299527784	0.87988150929206388
H16	2.2756479573933119	5.2356878814479098	-0.34278206342139567
H17	0.90991946343759211	4.5553243907743681	0.96302298382412788
H18	-2.5300396003515084	4.2590835330419621	-0.30335311087201583
H19	-1.0044651831277969	4.2048924170466870	0.98977747992716092
H20	2.9197986367034288	2.1844998046240476	-0.12506972159638427
H21	1.3622151093946622	2.4930902454242081	1.1088527064641973
B22	-2.2859986306344586	1.1337277599687376	0.89206643694050503
B23	1.2197822839744319	-0.58701750443155831	1.1024556776044738
B24	-0.72661411187457758	-2.2095763850558758	0.89158754487813052
B25	0.59965508991579741	-1.9122427296502844	-0.22130861041911939
B26	-0.87698579708734103	1.7484597052958373	1.7817948411029876
B27	-0.27406363709651366	-1.2361333433019217	2.1673234062278226
B28	0.34399752371344167	0.48204702959228757	2.1550618847178589
B29	-1.4712904465671259	0.12886590250915725	2.3073664797845144
H30	-0.95353203287170074	2.6511006515745361	2.5341679157440669
H31	2.4726114595534247 3E-002	-1.7962589147316343	3.1712220447653143
H32	1.0240918102360665	0.74462238077514631	3.0827702116677562
H33	-2.1206558728078191	9.6667048852804804 4E-002	3.2919056063986760
H34	-3.4256547428437032	1.4085034418881575	0.87770120733017820
H35	-1.8227808694884122	1.1156566480615222	-0.36353610646143580
H36	2.3674174034640623	-0.73180245862182502	1.3062948113030801
H37	1.0187208678125743	-0.71615141128284421	-0.22253334780303244
B38	-1.6144324945869404	-3.5910960776056213	0.15210576661080757
B39	-0.39148471984017047	-5.1347012796869240	-0.39975406846001987
B40	1.7111331088730408	-3.1450665773264395	-0.47433282265173743
B41	1.3594952690687925	-4.8943118019842551	3.1067138936257052 1E-002
B42	-1.0374951092555855	-2.1884526146980607	-0.83396012083850890
B43	0.80472996422257914	-4.3897962004698527	-1.5428924345445481
B44	-0.92860208140623679	-3.8516801784154109	-1.4827850339067474
B45	0.41364045775691716	-2.7196280407541433	-1.7606271962711515
H46	-1.7261278934375104	-1.3566394516198448	-1.3053700112410613
H47	1.2204722645247235	-4.9306631333905857	-2.5027199419566770
H48	-1.7026448449910589	-4.1919084503870732	-2.3011324346721902
H49	0.71354499461747023	-2.1831868466717537	-2.7634845081373700
H50	-0.96885775131677965	-3.4678828650620610	1.2833628164993929
H51	2.1418129061283238	-5.7414755321935251	0.25022709709425789
H52	-0.85615416043007142	-6.2131693190013060	-0.43463780429524040
H53	0.28160456701118047	-5.0921030808930023	0.75729428875743932
H54	2.8473826847412540	-2.8690541291093998	-0.62725300040188892
H55	1.6799952074594557	-3.8126255086002110	0.69903107441900103

H56 -2.7235194813703729 -3.8556794028858277 0.44029488836742020

3b (S_0 min) – B3LYP

B1	4.63820700	1.13586300	-0.34011300
B2	3.28664100	0.94583200	-1.50047700
B3	4.67480700	-0.41579000	0.60283100
B4	1.57649300	0.31516200	-0.66511700
B5	3.00398300	-1.11225800	1.36190200
B6	1.50722000	-0.07510000	1.10811000
B7	4.47658600	-0.34824200	-1.19808000
B8	1.90810900	-1.35600000	-0.04033400
B9	2.73502000	-0.71678800	-1.49719900
B10	3.64532500	-1.58023600	-0.21227400
H11	5.29097500	-0.70206200	-1.97292000
H12	1.20235000	-2.28814000	-0.17443200
H13	2.41015400	-1.15759800	-2.54292600
H14	4.04104100	-2.69142100	-0.25425300
H15	5.50056700	1.93546600	-0.38585700
H16	5.67869000	-0.70167800	1.15035500
H17	4.40841100	0.83854400	0.94675400
H18	3.20020500	1.64276600	-2.44666800
H19	3.49262800	1.77175400	-0.47541200
H20	3.04882200	-1.83769800	2.28926300
H21	2.65245300	0.06747300	1.81619400
B22	0.12534000	1.39234000	-0.91993100
B23	-0.15840600	-0.68135300	1.95944200
B24	-1.59957000	0.69010300	-0.17472900
B25	-1.49656500	-0.86279600	0.77435900
B26	1.20889500	1.60522100	0.47879500
B27	-1.33841700	0.61985400	1.65508900
B28	0.37030600	0.99619200	1.92903700
B29	-0.54361600	1.86287700	0.63201200
H30	-2.13426100	0.96469900	2.45291000
H31	0.67942500	1.44473500	2.97599500
H32	-0.91667700	2.97863300	0.70951500
H33	0.07603800	2.10724600	-1.85381000
H34	0.44926600	0.19556500	-1.36885500
H35	-0.11518400	-1.32561100	2.94505600
H36	-0.35720400	-1.52494700	0.96470000
B37	-2.80157200	-1.95417100	0.15609700
B38	-3.45211500	1.48561400	-0.32207900
B39	-4.56375200	-1.12424500	0.09504000
B40	-4.74059700	0.61747400	0.57443300
B41	-1.76347500	-0.97310500	-0.93998100
B42	-4.48694000	0.24598400	-1.08840700
B43	-2.74145500	0.42210500	-1.51314800
B44	-3.47332600	-1.20038300	-1.29015100
H45	-0.95324200	-1.45341000	-1.64709500
H46	-5.31447900	0.47467100	-1.89590000
H47	-2.46080900	0.90782800	-2.55103800

H48	-3.75443000	-1.97196700	-2.13803000
H49	-2.69492200	-3.12383200	0.25244800
H50	-5.67938400	1.10349000	1.09167900
H51	-3.51762900	2.65339500	-0.46128400
H52	-3.66360000	1.26993000	0.97410800
H53	-5.49481500	-1.83366800	0.23435400
H54	-4.41553700	-0.48437300	1.25281500
H55	1.92234400	2.52810300	0.63725200
H56	-2.56682900	-1.45866600	1.34945400

3b (S_1 min) – CASSCF

B1	4.70919471	1.19190009	-0.33431868
B2	3.21591336	1.01651282	-1.45497309
B3	4.71956182	-0.40793028	0.60717739
B4	1.68104845	0.46511089	-0.65106093
B5	3.14037614	-1.03620873	1.39177258
B6	1.58978850	0.04142425	1.13430885
B7	4.45826701	-0.32024946	-1.21782137
B8	1.89327114	-1.25786811	0.01860910
B9	2.75090005	-0.73754650	-1.52354471
B10	3.64316314	-1.58987851	-0.22612599
H11	5.26435033	-0.66295392	-2.00495051
H12	1.15340352	-2.14864952	-0.19205209
H13	2.36738594	-1.21342489	-2.52784943
H14	4.01673097	-2.70517741	-0.26575189
H15	5.68237103	1.81858943	-0.54127139
H16	5.75235166	-0.74327113	1.06245663
H17	4.55528329	0.89939572	0.93394288
H18	3.18611858	1.70860804	-2.40858185
H19	3.66420863	1.89668370	-0.40563580
H20	3.14995368	-1.71305206	2.35468004
H21	2.64742107	0.18122011	1.83786638
B22	0.08927395	1.50021833	-0.85271781
B23	-0.04075354	-0.77364767	1.89376788
B24	-1.62272637	0.67160747	-0.16469987
B25	-1.48679539	-0.93053762	0.68461014
B26	1.16086924	1.73008753	0.61504991
B27	-1.36951003	0.51848726	1.69508015
B28	0.30508943	0.98793890	2.01409252
B29	-0.58933313	1.88019062	0.73626561
H30	-2.17722433	0.71234904	2.52677741
H31	0.57526905	1.39580560	3.08347037
H32	-1.04486751	2.95523941	0.86901924
H33	-0.00962153	2.26864601	-1.73494137
H34	0.53630249	0.37377809	-1.33172927
H35	0.06176959	-1.51204141	2.79961975
H36	-0.43302837	-1.60785256	0.85001657
B37	-2.79068925	-2.02946087	-0.02230982
B38	-3.51453416	1.43742894	-0.20855621
B39	-4.59647249	-1.23866787	-0.01773753

B40	-4.78643550	0.45703998	0.63096478
B41	-1.75375574	-0.92588642	-1.05364312
B42	-4.54549550	0.23870561	-1.08169593
B43	-2.79575196	0.49414170	-1.50779721
B44	-3.48615795	-1.17485011	-1.40958938
H45	-0.94029329	-1.34994118	-1.78604570
H46	-5.37802988	0.51790123	-1.86335194
H47	-2.54968070	1.08211221	-2.49490635
H48	-3.76335643	-1.88941277	-2.30182161
H49	-2.64683407	-3.19377309	0.02421384
H50	-5.72068261	0.87484769	1.20387157
H51	-3.61130612	2.60662085	-0.24474523
H52	-3.71304150	1.09339231	1.05592827
H53	-5.51404921	-1.96951777	0.05245578
H54	-4.43413981	-0.71053336	1.18429759
H55	1.84384592	2.65492316	0.85054084
H56	-2.48742331	-1.56519278	1.21886899

3b (S_0/S_1 CI) – CASSCF

B1	4.09544964	1.15221953	-1.94210288
B2	2.56535848	0.35374962	-2.50662371
B3	4.72591275	0.13107850	-0.59439869
B4	1.34204083	-0.09752838	-1.00958508
B5	3.55530134	-0.24461009	0.73419789
B6	1.82692620	0.40629936	0.63062714
B7	4.05000959	-0.57569751	-2.14396116
B8	2.20276232	-1.26174010	0.12034564
B9	2.43689740	-1.24390718	-1.75590129
B10	3.80887708	-1.36147432	-0.58534059
H11	4.70628053	-1.11033703	-2.96004331
H12	1.77258626	-2.19807334	0.67559918
H13	1.99942208	-2.08286683	-2.45033136
H14	4.46090435	-2.30766322	-0.33577546
H15	4.74057570	1.92724915	-2.54186378
H16	5.85962526	0.23008811	-0.30081941
H17	4.24929809	1.37082074	-0.64918215
H18	2.09914557	0.58658979	-3.55678885
H19	2.82974298	1.54211422	-1.96883997
H20	4.03902137	-0.46653181	1.78358342
H21	3.02136101	0.94236719	0.83200537
B22	-0.28811082	0.71744973	-1.26734149
B23	0.43368646	0.18147146	2.13913280
B24	-1.67394366	0.47667146	0.18845700
B25	-1.20272978	-0.45341327	1.69181261
B26	1.11323894	1.55876062	-0.52154953
B27	-0.90611129	1.28448589	1.66252301
B28	0.78142484	1.67246635	1.23387889
B29	-0.52263250	1.89673727	0.04051545
H30	-1.45579255	2.01361328	2.40208866

H31	1.30652039	2.53478346	1.83994508
H32	-1.00629265	2.91925833	-0.27485376
H33	-0.66417790	0.89878763	-2.36395754
H34	0.10241545	-0.55277324	-1.21175898
H35	0.84503603	0.01628271	3.22708197
H36	-0.01842766	-1.00219243	1.70608312
B37	-3.16828597	-2.44166356	1.23847294
B38	-3.51779653	1.21123486	0.23336782
B39	-4.17247625	-1.34611938	1.62540422
B40	-4.55191557	0.57219353	1.61067310
B41	-2.01018324	-1.32990242	0.10918421
B42	-4.70195321	-0.10478989	0.02892519
B43	-3.13619503	-0.14954406	-0.75050132
B44	-3.80048132	-1.63760034	-0.09303299
H45	-1.29526250	-2.09059726	-0.44471844
H46	-5.66891042	-0.04307269	-0.63757918
H47	-3.04442618	-0.04887616	-1.91562643
H48	-4.17932449	-2.42448840	-0.89050402
H49	-3.09523297	-3.60743968	1.31040433
H50	-5.40204080	1.10708676	2.21808052
H51	-3.64367561	2.30747000	-0.16559282
H52	-3.47891982	1.28220456	1.58070081
H53	-4.33038609	-2.21938579	2.41393739
H54	-3.93756004	-0.27619443	2.41104464
H55	1.72216151	2.44551478	-1.00421049
H56	-1.80724462	-0.79718506	2.65421131

3c (S_0 min) – B3LYP

B1	-4.67368000	0.99007100	-0.35651600
B2	-3.51226700	1.08093000	1.00694400
B3	-4.53134600	-0.70772600	-0.98980800
B4	-1.64544800	0.41811300	0.60086400
B5	-2.76229500	-1.45526300	-1.34713100
B6	-1.40620200	-0.28825000	-1.06010400
B7	-4.61519100	-0.30670400	0.77554600
B8	-1.87803300	-1.36675800	0.21829800
B9	-2.93380100	-0.51984500	1.39683900
B10	-3.61455700	-1.65287400	0.18434700
H11	-5.53505000	-0.54968800	1.47031000
H12	-1.15243800	-2.21607900	0.59070600
H13	-2.78332400	-0.75409700	2.54334700
H14	-3.98621100	-2.75615000	0.37742000
H15	-5.55192800	1.74077100	-0.58178500
H16	-5.42976800	-1.13689200	-1.62078900
H17	-4.25086800	0.48294300	-1.51782000
H18	-3.60662800	1.94013400	1.80718900
H19	-3.56990000	1.69197700	-0.17436500
H20	-2.63078600	-2.34801400	-2.10499900
H21	-2.39435400	-0.36574800	-1.98045000

B22	0.05462100	0.48547400	-1.77434900
B23	1.64545500	0.41812200	-0.60085800
B24	-0.05462800	0.48546800	1.77434500
B25	1.40620700	-0.28825200	1.06010400
B26	-1.18560200	1.41981800	-0.88859600
B27	1.18559800	1.41981500	0.88859800
B28	0.53647800	1.81051900	-0.72604600
B29	-0.53647700	1.81052100	0.72604500
H30	-1.90479300	2.19039900	-1.41651800
H31	1.90478800	2.19040000	1.41651800
H32	0.92483500	2.77785000	-1.27715600
H33	-0.92483700	2.77784700	1.27716100
H34	0.20043500	0.53530900	-2.94229900
H35	-0.23657600	-0.77022700	-1.48459000
H36	-0.20043600	0.53530100	2.94229600
H37	0.23658000	-0.77023000	1.48459300
B38	2.76229300	-1.45526500	1.34712800
B39	4.53135000	-0.70773000	0.98980300
B40	3.51226100	1.08093200	-1.00693600
B41	4.67368500	0.99007000	0.35651900
B42	1.87803000	-1.36675800	-0.21830200
B43	4.61518700	-0.30670200	-0.77554500
B44	3.61455700	-1.65287500	-0.18434900
B45	2.93380100	-0.51984400	-1.39684200
H46	1.15243100	-2.21607700	-0.59070500
H47	5.53504200	-0.54968800	-1.47031400
H48	3.98621000	-2.75615000	-0.37742400
H49	2.78332000	-0.75408500	-2.54335100
H50	2.63078500	-2.34801600	2.10499700
H51	2.39435800	-0.36574400	1.98044500
H52	5.55193600	1.74076800	0.58178400
H53	5.42977600	-1.13690100	1.62077600
H54	4.25087800	0.48293800	1.51782300
H55	3.60662800	1.94013800	-1.80717800
H56	3.56990600	1.69197900	0.17437400

3c (S_1 min) – CASSCF

B1	-4.70804552	0.99518266	-0.39280414
B2	-3.48514469	1.16449796	0.95977897
B3	-4.59593019	-0.77684808	-0.89397404
B4	-1.68796678	0.47996404	0.60078645
B5	-2.86549703	-1.52476578	-1.23529985
B6	-1.43274954	-0.33875836	-1.02131009
B7	-4.66082140	-0.22358119	0.84798628
B8	-1.89803173	-1.35936135	0.33010459
B9	-2.98134988	-0.43258875	1.50059354
B10	-3.65784879	-1.63484039	0.37129013
H11	-5.57843652	-0.39465639	1.56458425
H12	-1.18047563	-2.20646931	0.71229162

H13	-2.82206698	-0.59687920	2.65317716
H14	-4.02770597	-2.72110568	0.63475588
H15	-5.60322480	1.71797638	-0.62689325
H16	-5.52525103	-1.25194543	-1.43749376
H17	-4.32772701	0.37706604	-1.50824828
H18	-3.57589084	2.08150121	1.68992654
H19	-3.61723699	1.68519041	-0.28296183
H20	-2.71755000	-2.43833061	-1.95914025
H21	-2.36120103	-0.42300555	-1.90493457
B22	0.13030222	0.45682410	-1.76643505
B23	1.65303856	0.40856472	-0.64134622
B24	-0.15543163	0.48391810	1.75334809
B25	1.41193478	-0.35732776	1.00456148
B26	-1.19240982	1.42144834	-0.93199959
B27	1.20510259	1.40633195	0.87448431
B28	0.50740297	1.86790431	-0.76976160
B29	-0.50748318	1.88879919	0.70718102
H30	-1.90912383	2.15414488	-1.50515794
H31	1.93111310	2.10870835	1.47491778
H32	0.91623210	2.83821749	-1.29052045
H33	-0.87395868	2.87812142	1.22426618
H34	0.26210509	0.41903970	-2.93325626
H35	-0.34934639	-0.84399244	-1.42084204
H36	-0.28508653	0.44473366	2.91862886
H37	0.35280678	-0.85463102	1.44019558
B38	2.84882861	-1.51616876	1.27238546
B39	4.61287871	-0.73091288	0.91844871
B40	3.47271498	1.12370745	-0.99708665
B41	4.68959065	1.01268589	0.36919187
B42	1.91488984	-1.41118198	-0.31279977
B43	4.66288984	-0.24692108	-0.83914778
B44	3.68201049	-1.65376958	-0.29525060
B45	2.99260305	-0.49604804	-1.48121116
H46	1.21631650	-2.27669444	-0.68713499
H47	5.58412727	-0.42690404	-1.54779475
H48	4.08104231	-2.73898484	-0.51715394
H49	2.84777469	-0.70450093	-2.62825165
H50	2.73425871	-2.39901529	2.03790759
H51	2.34063910	-0.40613032	1.89819647
H52	5.56237300	1.76212743	0.60033215
H53	5.53419014	-1.17461342	1.49857946
H54	4.30119468	0.42058389	1.50250922
H55	3.54733900	2.01986306	-1.75282294
H56	3.58729966	1.68380518	0.22061777

3c (S_0/S_1 CI) – CASSCF

B1	-4.741701	0.613642	-0.990658
B2	-3.676850	0.527033	0.463825
B3	-4.405571	-0.799248	-2.382247

B4	-1.729700	0.182731	0.166609
B5	-3.308925	-1.808325	-1.844444
B6	-1.150080	0.106729	-1.585470
B7	-4.625977	-0.874008	-0.022253
B8	-1.688963	-1.394688	-0.642396
B9	-2.870090	-1.089159	0.694346
B10	-3.166398	-2.507877	-0.376999
H11	-5.592646	-1.356375	0.425887
H12	-0.864079	-2.245614	-0.645839
H13	-2.849982	-1.422544	1.822558
H14	-3.260049	-3.532949	0.181355
H15	-5.715582	1.271183	-1.026772
H16	-4.941035	-0.771138	-3.458214
H17	-4.270065	0.557441	-2.212458
H18	-3.983253	1.151060	1.408486
H19	-3.691192	1.313607	-0.592460
H20	-5.142177	-1.701031	-1.863524
H21	-1.661545	0.164093	-2.645986
B22	0.389012	1.148879	-1.592374
B23	1.780915	0.778876	-0.175843
B24	-0.357192	-0.064361	1.706916
B25	1.322298	-0.449263	1.097890
B26	-1.126095	1.658760	-0.749068
B27	0.927182	1.213054	1.415354
B28	0.535383	2.076648	-0.106001
B29	-0.815291	1.527983	0.996841
H30	-1.819448	2.531948	-1.127968
H31	1.434648	1.788009	2.309080
H32	0.902980	3.188201	-0.235560
H33	-1.421588	2.217662	1.733441
H34	0.761798	1.587542	-2.618911
H35	0.157277	-0.132611	-1.738714
H36	-0.734052	-0.416485	2.761221
H37	0.183896	-1.117156	1.114415
B38	2.750550	-1.607904	1.301770
B39	4.465662	-0.723837	1.552013
B40	3.613356	1.602299	0.003254
B41	4.542864	1.137217	1.513357
B42	2.127754	-1.059352	-0.323874
B43	4.877995	0.271652	0.047657
B44	3.873529	-1.284564	-0.014308
B45	3.278936	0.158709	-0.961470
H46	1.573562	-1.786844	-1.061508
H47	5.936287	0.322287	-0.459674
H48	4.385323	-2.244347	-0.459863
H49	3.349233	0.298495	-2.126831
H50	2.591590	-2.693364	1.721021
H51	2.138195	-0.777562	2.128615
H52	5.263363	1.800467	2.154166
H53	5.283597	-1.294188	2.176489
H54	3.960354	0.232186	2.321607

H55	3.779405	2.658432	-0.482173
H56	3.422585	1.807947	1.305686

References

1 B. O. Roos, P. R. Taylor and P. E. M. Siegbahn, *Chem. Phys.*, 1980, **48**, 157–173.

2 F. Aquilante, J. Autschbach, R. K. Carlson, L. F. Chibotaru, M. G. Delcey, L. De Vico, I. Fdez. Galván, N. Ferré, L. M. Frutos, L. Gagliardi, M. Garavelli, A. Giussani, C. E. Hoyer, G. Li Manni, H. Lischka, D. Ma, P. Å. Malmqvist, T. Müller, A. Nenov, M. Olivucci, T. B. Pedersen, D. Peng, F. Plasser, B. Pritchard, M. Reiher, I. Rivalta, I. Schapiro, J. Segarra-Martí, M. Stenrup, D. G. Truhlar, L. Ungur, A. Valentini, S. Vancoillie, V. Veryazov, V. P. Vysotskiy, O. Weingart, F. Zapata and R. Lindh, *J. Comput. Chem.*, 2015, **37**, 506–541.

3 L. De Vico, M. Olivucci and R. Lindh, *J. Chem. Theory Comput.*, 2005, **1**, 1029–1037.

4 K. Andersson, P. Å. Malmqvist, B. O. Roos, A. J. Sadlej and K. Wolinski, *J. Phys. Chem.*, 1990, **94**, 5483–5488.

5 K. Andersson, P. Å. Malmqvist and B. O. Roos, *J. Chem. Phys.*, 1992, **96**, 1218–1226.

6 M. G. S. Londesborough, D. Hnyk, J. Bould, L. Serrano-Andrés, V. Sauri, J. M. Oliva, P. Kubat, T. Polivka and K. Lang, *Inorg. Chem.*, 2012, **51**, 1471–1479.

7 V. Sauri, J. M. Oliva, D. Hnyk, J. Bould, J. Braborec, M. Merchan, P. Kubat, I. Cisarova, K. Lang and M. G. S. Londesborough, *Inorg. Chem.*, 2013, **52**, 9266–9274.

8 M. G. S. Londesborough, J. Dolanský, L. Cerdán, K. Lang, T. Jelínek, J. M. Oliva, D. Hnyk, D. Roca-Sanjuán, A. Francés-Monerris, J. Martinčík, M. Nikl and J. D. Kennedy, *Adv. Opt. Mater.*, 2017, **5**, 1600694.

9 M. G. S. Londesborough, J. Dolansky, T. Jelinek, J. D. Kennedy, I. Cisarova, R. D. Kennedy, D. Roca-Sanjuán, A. Francés-Monerris, K. Lang and W. Clegg, *Dalt. Trans.*, 2018, **47**, 1709–1725.

10 J. M. Oliva, A. Francés-Monerris and D. Roca-Sanjuán, in *Boron: The Fifth Element*, eds. D. Hnyk and M. McKee, Springer International Publishing, Cham, 2015, pp. 97–119.

11 M. Barbatti, M. Ruckenbauer, F. Plasser, J. Pittner, G. Granucci, M. Persico and H. Lischka, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2013, **4**, 26–33.