Unravelling electronic structure, bonding and magnetic properties in inorganic dysprosocene analogues $[Dy(E_4)_2]^{2-}$ (where E= N, P, As, CH)

*Ibtesham Tarannum, Saurabh Kumar Singh**

Computational Inorganic Chemistry Group, Department of Chemistry, Indian Institute of Technology Hyderabad, Kandi, Sangareddy, Telangana, India-502284

Table of Contents

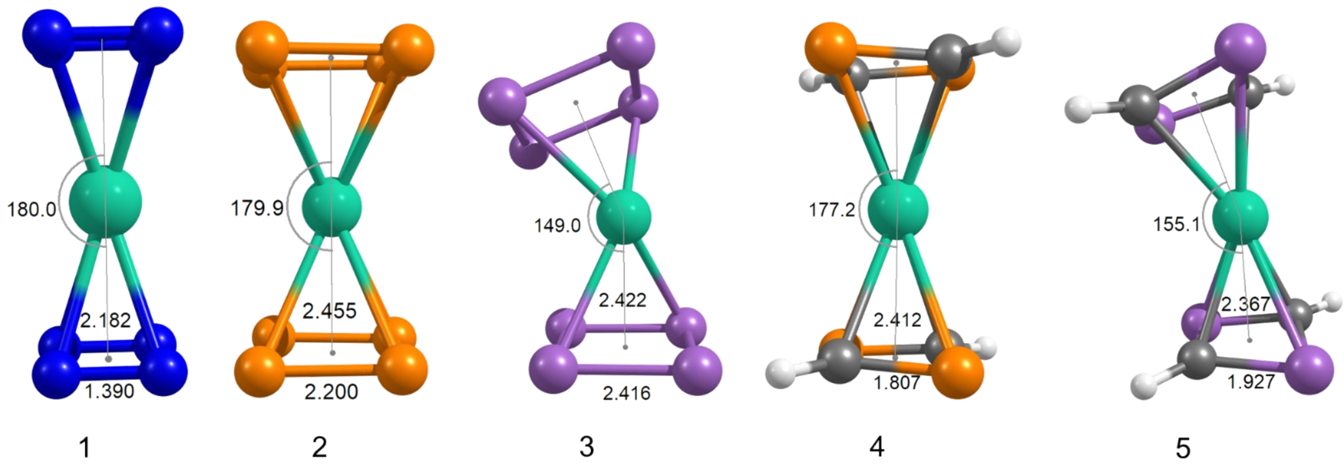


Figure S1: DFT optimized geometry of $[Dy(E_4)_2]^-$ complexes at DKH/BP86 level of theory.

Table S1: Comparison of selected structural parameters of a previously reported complex $[Dy(N_5)]^+$ complex.

$[Dy(N_5)_2]^+$	Reported*	Optimized #
Avg. N-N (Å)	1.332	1.338
Dy-L$_c$ (Å)	2.225	2.242
∠ L$_{cent}$-Dy-L$_c$ (°)	153.5	158.2

*Reported Geometry (*Inorg. Chem. 2019, 58, 14046−14057*) calculation was performed using ORCA/4.1 at meta-GGA TPSSh level of theory and SARC2-ZORA-QZV for Dy and ZORA-def2-TZVP for Nitrogen(N).

#Calculation was performed using ORCA/4.2.1 at GGA BP86 level of theory and SARC2-DKH-TZVP for Dy DKH-def2-SVP for Nitrogen(N).

Table S2: Comparison of selected structural parameters of complexes **1-5** optimized at BP86 level of theory.

Complexes	Bond Length (Å)		Bond Angle (°)
	Avg. E-E	Dy-L$_{cent}$	L$_{cent}$-Dy-L$_{cent}$
1	1.393	2.182	180.0
2	2.200	2.470	179.9
3	2.416	2.422	149.0
4	1.807	2.412	177.2
5	1.927	2.367	155.1
$[Dy(Cb)_2]^-$	1.444	2.339	179.9*
$[Dy(Cp^*)_2]^+$	1.442	2.273	148.0

*data taken from ref; *Dalton Trans.*, 2023, **52**, 15576-15589

Table S3: EDA analysis for $[Dy(E_4)_2]^-$ complexes. All the values provided here are in the kcal.mol^{-1}.

Parameters	1	2	3	4	5
Pauli Energy (ΔE_{Pauli})	207.0	172.4	208.5	176.5	202.0
Electrostatic Energy (ΔE_{elec})	-1475.5	-1134.4	-1126.4	-1245.5	-1234.5
Orbital Interaction (ΔE_{orb})	-469.1	-587.8	-624.0	-568.9	-608.7
Dispersion (ΔE_{disp})	-2.5	-4.5	-5.1	-4.2	-4.1
Total Bonding Energy (ΔE_{int})	-1740.1	-1554.3	-1547.1	-1642.0	-1645.3

Table S4: Percentage contribution of the decomposed energies to the total bonding energy for $[Dy(E_4)_2]^-$ complexes.

Complexes	ΔE_{Pauli} (%)	ΔE_{elec} (%)	ΔE_{orb} (%)	ΔE_{disp} (%)
1	11.9	84.8	27.0	0.1
2	11.1	73.0	37.8	0.3
3	13.5	72.8	40.3	0.3
4	10.8	75.9	34.6	0.3
5	12.3	75.0	37.0	0.3
% contribution to total binding energy = $(E/E_{tot}) * 100$				

Table S5: EDA analysis of complexes **1-5** with fragmentation scheme $((Dy(E_4))^+ + (E_4)^{2-})$. All the values provided here are in the kcal.mol^{-1}.

Parameters	1	2	3	4	5
Pauli Repulsion (ΔE_{Pauli})	123.2	107.9	137.1	112.7	133.0
Electrostatic Energy (ΔE_{elec})	-390.3	-293.0	-300.9	-321.3	-324.3
Orbital Interaction (ΔE_{orb})	-133.1	-134.6	-142.4	-134.2	-142.9
Dispersion (ΔE_{disp})	-1.7	-4.5	-6.7	-3.3	-4.1
Total Bonding Energy (ΔE_{int})	-401.9	-324.2	-312.8	-346.2	-338.3

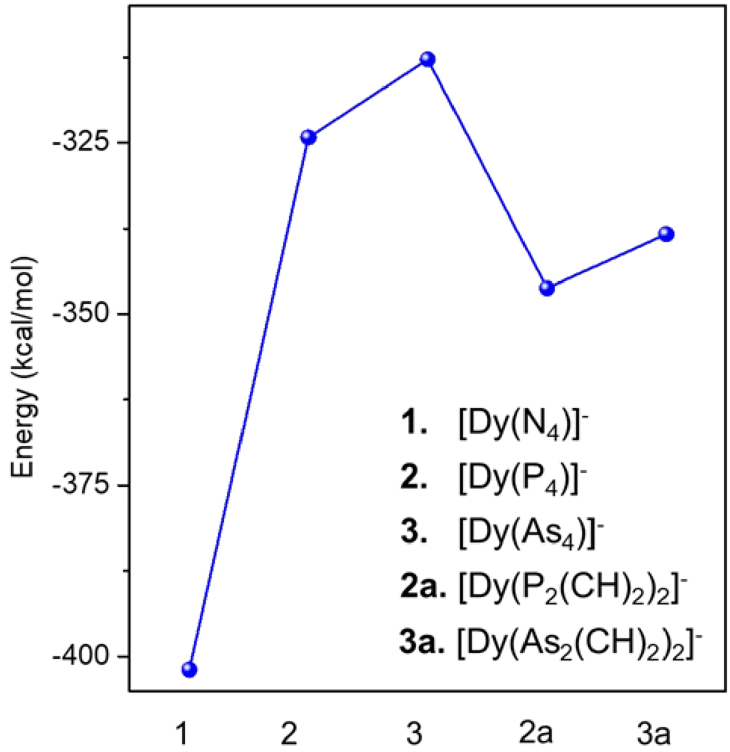


Figure S2: DFT computed trends in the total binding energy for complexes **1-5** using fragmentation scheme $((Dy(E_4))^{+} + (E_4)^{2-})$.

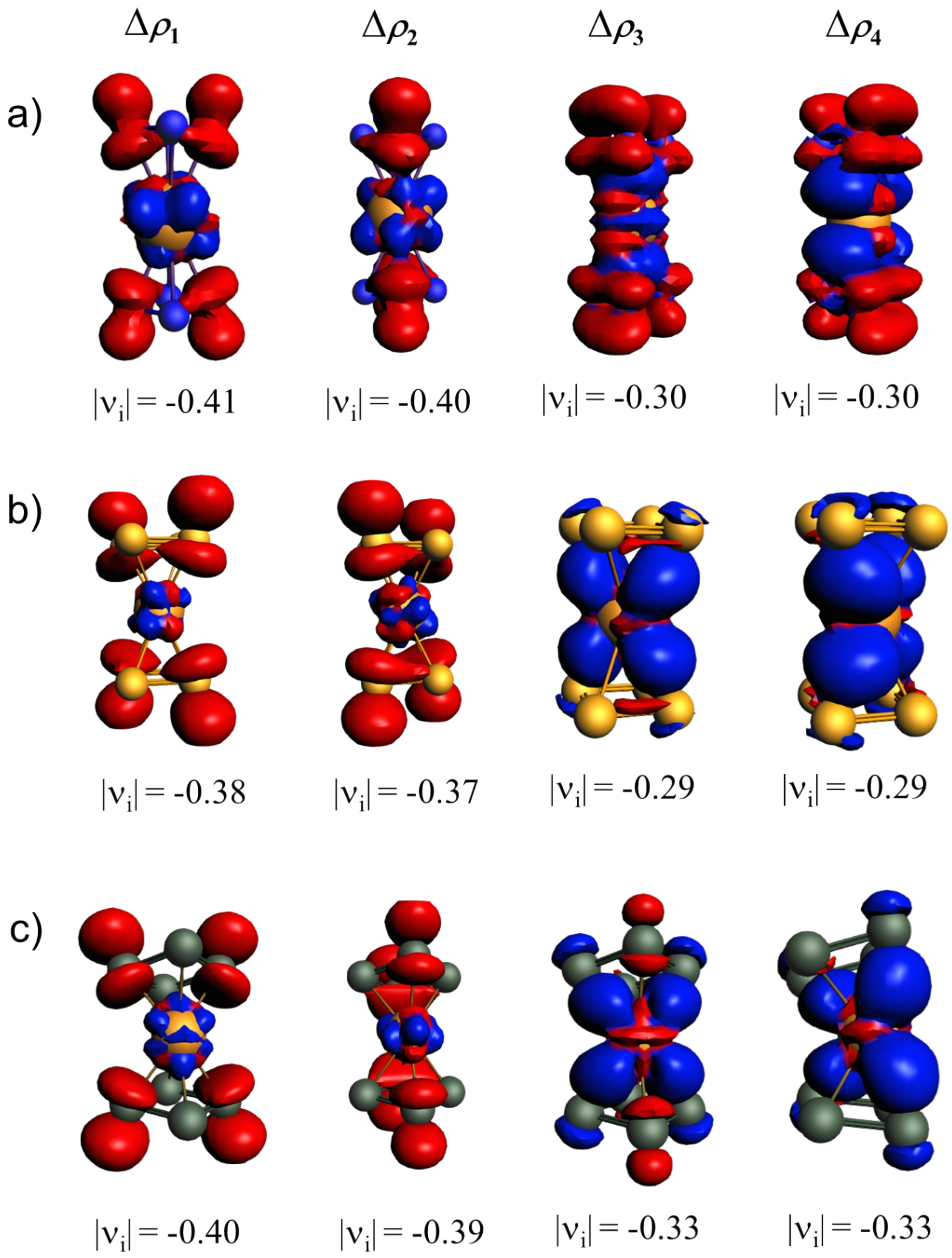


Figure S3: The first four electron deformation densities, $\Delta E_{orb(n)}$, along with their eigenvalues for complexes a) **1**, b) **2**, c) **3**. The $\Delta E_{orb(n)}$ energies are in kcal/mol.

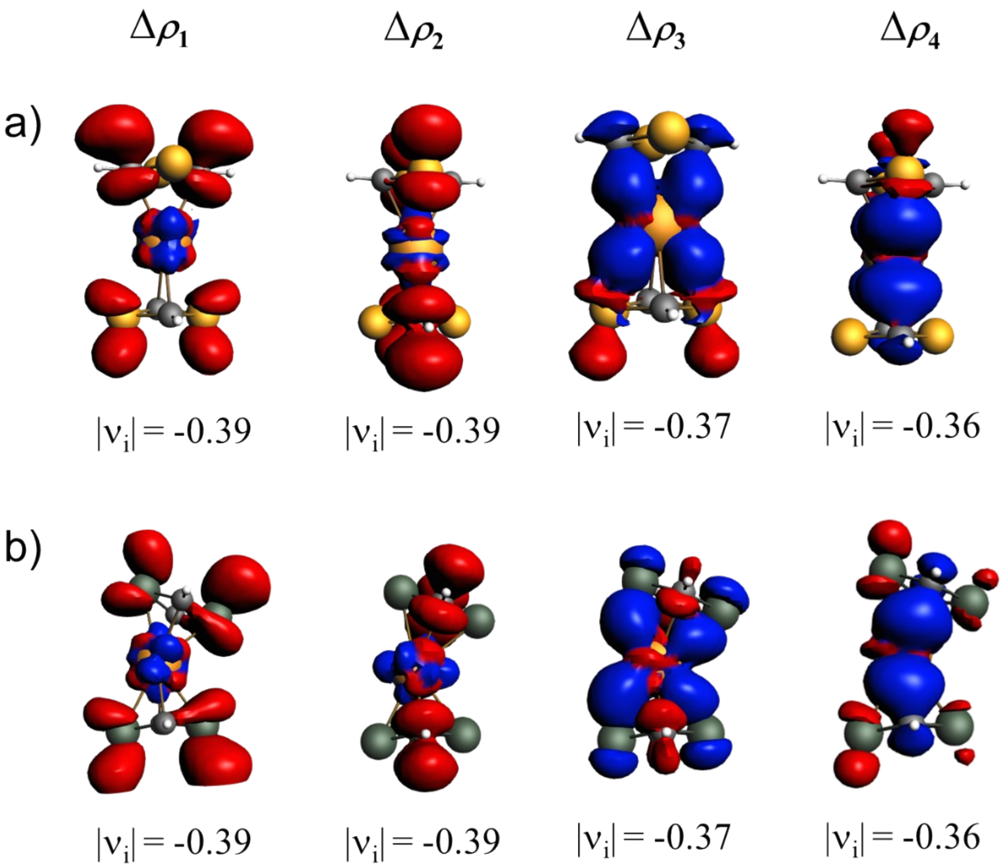
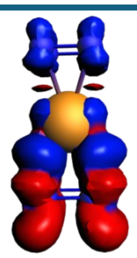
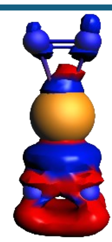


Figure S4: The first four electron deformation densities, $\Delta E_{orb(n)}$, along with their eigenvalues for complexes a) **4**, b) **5**. The $\Delta E_{orb(n)}$ energies are in kcal/mol.

Table S6: The shape of the first three highest electron deformation densities, $\Delta E_{orb(1)\text{-}(3)}$ for **1-5** with fragmentation scheme $((Dy(E_4))^+ + (E_4)^{2-})$. Isosurface values are 0.0003 au. The ΔE_{orb} energies are in kcal.mol^{-1}.

Complexes	$\Delta \boldsymbol{E}_{\mathbf{orb(1)}}$	$\Delta \boldsymbol{E}_{\mathbf{orb(2)}}$	$\Delta \boldsymbol{E}_{\mathbf{orb(3)}}$
1	 $\Delta\rho_{(\pi)}$ $\Delta E_{orb(1)}$ =-17.1; $\lvert\nu_1\rvert$=-0.25	 $\Delta\rho_{(\pi)}$ $\Delta E_{orb(1)}$ =-17.1; $\lvert\nu_1\rvert$=-0.25	 $\Delta\rho_{(\sigma)}$ $\Delta E_{orb(1)}$ =-7.5; $\lvert\nu_1\rvert$ =-0.13

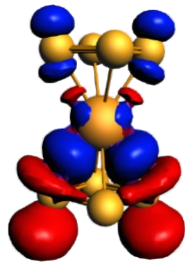
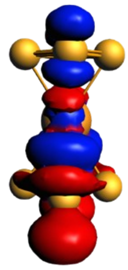
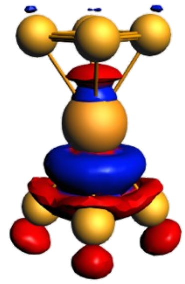
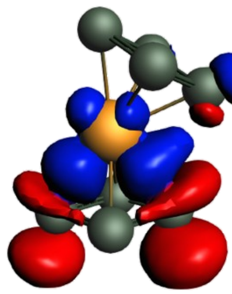
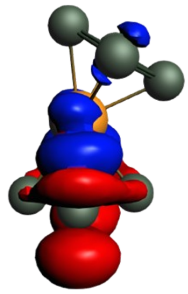
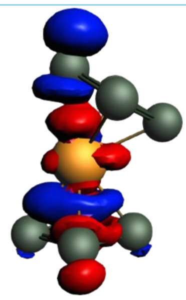
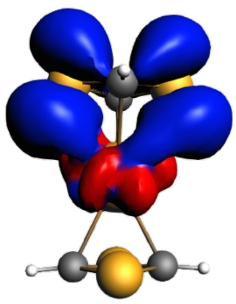
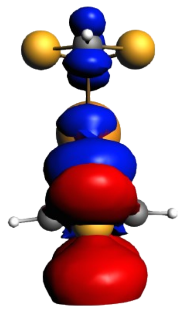
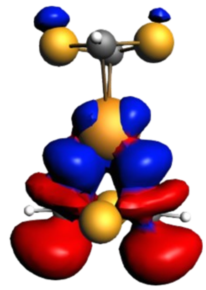
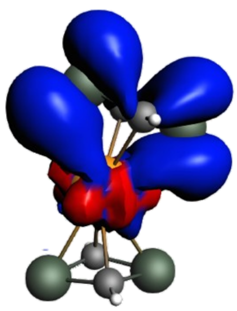
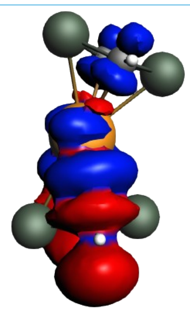
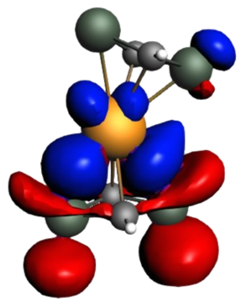
2	 $\Delta\rho_{(\pi)}$ $\Delta E_{\mathrm{orb}(1)}$ =-17.1; $\lvert\nu_1\rvert$=-0.29	 $\Delta\rho_{(\pi)}$ $\Delta E_{\mathrm{orb}(1)}$ =-16.2; $\lvert\nu_1\rvert$=-0.29	 $\Delta\rho_{(\sigma)}$ $\Delta E_{\mathrm{orb}(1)}$ =-9.2; $\lvert\nu_1\rvert$=-0.17
3	 $\Delta\rho_{(\pi)}$ $\Delta E_{\mathrm{orb}(1)}$ =-17.7; $\lvert\nu_1\rvert$=-0.31	 $\Delta\rho_{(\pi)}$ $\Delta E_{\mathrm{orb}(1)}$ =-16.9; $\lvert\nu_1\rvert$=-0.29	 $\Delta\rho_{(\sigma)}$ $\Delta E_{\mathrm{orb}(1)}$ =-7.4; $\lvert\nu_1\rvert$ =-0.18
4	 $\Delta\rho_{(\pi)}$ $\Delta E_{\mathrm{orb}(1)}$ =-19.0; $\lvert\nu_1\rvert$=-0.61	 $\Delta\rho_{(\pi)}$ $\Delta E_{\mathrm{orb}(1)}$ =-16.8; $\lvert\nu_1\rvert$=-0.31	 $\Delta\rho_{(\pi)}$ $\Delta E_{\mathrm{orb}(1)}$ =-14.3; $\lvert\nu_1\rvert$ =-0.26
5	 $\Delta\rho_{(\pi)}$ $\Delta E_{\mathrm{orb}(1)}$ =-20.1; $\lvert\nu_1\rvert$=-0.63	 $\Delta\rho_{(\pi)}$ $\Delta E_{\mathrm{orb}(1)}$ =-15.8; $\lvert\nu_1\rvert$=-0.28	 $\Delta\rho_{(\pi)}$ $\Delta E_{\mathrm{orb}(1)}$ =-15.4; $\lvert\nu_1\rvert$ =-0.32

Table S7. Percentage metal contribution (%) to Dy-E bonding NLMOs in complexes **1-5**. The major dominating compositions are in bold.

Complexes	%M	M (s+p)	M (d)	M (f)
1	8.4	1.6	**6.6**	0.2
2	9.7	1.1	**6.7**	1.9
3	10.9	0.4	**8.0**	2.4
4	8.4	0.9	**6.2**	1.3
5	8.2	0.8	**5.5**	1.9

Table S8. DFT computed the NPA population of various valence Dy(III) orbitals in complexes **1-5**.

Complexes	4f	5d	6p
1	9.07	0.88	0.03
2	9.06	1.04	0.06
3	9.03	1.28	0.03
4	9.05	0.96	0.08
5	9.03	1.12	0.05

Table S9: AILFT computed the Slater Condon parameters F^2, F^4, and F^6, the one-electron effective parameters for spin-orbit coupling (ζ) for complexes **1-5** at NEVPT2 level of theory. The values in the parenthesis are the CASSCF computed values. All the values provided here are in the cm^{-1}.

	Dy(III) ion	1	2	3	4	5
F^2	109690.9 (121962.8)	107521.2 (120860.3)	107443.4 (120938.3)	107263.5 (120867.9)	107380.8 (120884.0)	107193.9 (120794.4)
F^4	70551.8 (76517.7)	70173.3 (75631.5)	70136.7 (75740.7)	70125.3 (75725.1)	70173.6 (75680.0)	70213.5 (75641.6)
F^6	55412.5 (55041.9)	54747.9 (54465.2)	54859.3 (54507.2)	54819.6 (54490.4)	54814.2 (54477.4)	54755.1 (54447.3)
ζ	1742.2	1733.7	1732.3	1731.4	1732.3	1731.2

Table S10: AILFT computed the Racah parameters E^1, E^2, and E^3 for complexes **1-5** at the NEVPT2 level of theory. The values in the parenthesis are the CASSCF computed values. All the values provided here are in the cm^{-1}.

	Dy(III) ion	1	2	3	4	5
E^1	7129.0 (7682.6)	7025.0 (7606.2)	7024.8 (7612.7)	7017.1 (7609.4)	7022.2 (7608.5)	7014.9 (7603.6)
E^2	38.4 (42.6)	37.4 (42.3)	37.4 (42.3)	37.3 (42.3)	37.3 (42.3)	37.2 (42.3)

E^3	713.8 (817.2)	699.7 (809.7)	698.6 (810.3)	697.5 (809.9)	698.4 (810.0)	697.4 (809.3)

Table S11: Reduction (%) in Slater Condon parameter F^2, F^4, and F^6 and Racah parameters E^1, E^2, and E^3 for complexes **1-5** at NEVPT2 level of theory. The values in the parenthesis are the CASSCF computed values.

	F^2(%)	**F^4(%)**	**F^6(%)**	**ζ(%)**	**E^1(%)**	**E^2(%)**	**E^3(%)**
1	2.0 (0.9)	0.5 (1.2)	1.2 (1.0)	0.5	1.5 (1.0)	2.7 (0.8)	2.0 (0.9)
2	2.0 (0.8)	0.6 (1.0)	1.0 (1.0)	0.6	1.5 (0.9)	2.7 (0.8)	2.1 (0.8)
3	2.2 (0.9)	0.6 (1.0)	1.1 (1.0)	0.6	1.6 (1.0)	2.9 (0.8)	2.3 (0.9)
4	2.1 (0.9)	0.5 (1.1)	1.1 (1.0)	0.6	1.5 (1.0)	2.8 (0.8)	2.1 (0.9)
5	2.3 (1.0)	0.5 (1.1)	1.2 (1.1)	0.6	1.6 (1.0)	3.1 (0.9)	2.3 (1.0)
Reduction (%) = [1- (complex/free-ion)] * 100							

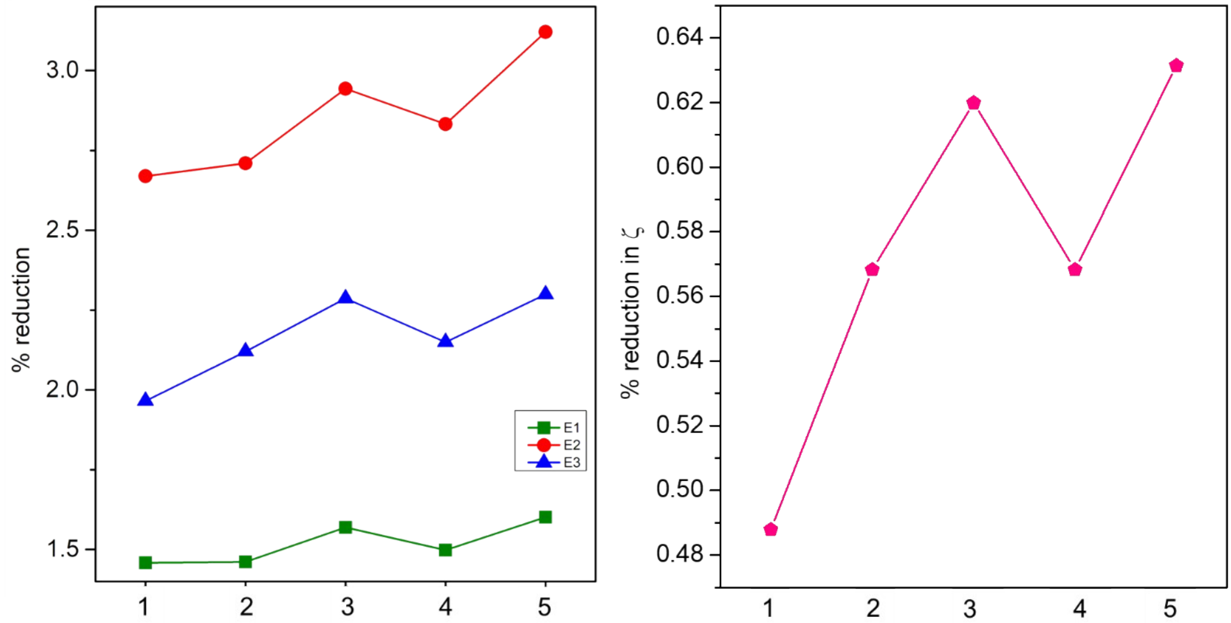


Figure S5: AILFT computed trends in the reduction (%) in Racah parameters (E^1, E^2, E^3) (left) and Spin-Orbit Coupling parameters (ζ) (right) for complexes **1-5** at NEVPT2 level of theory.

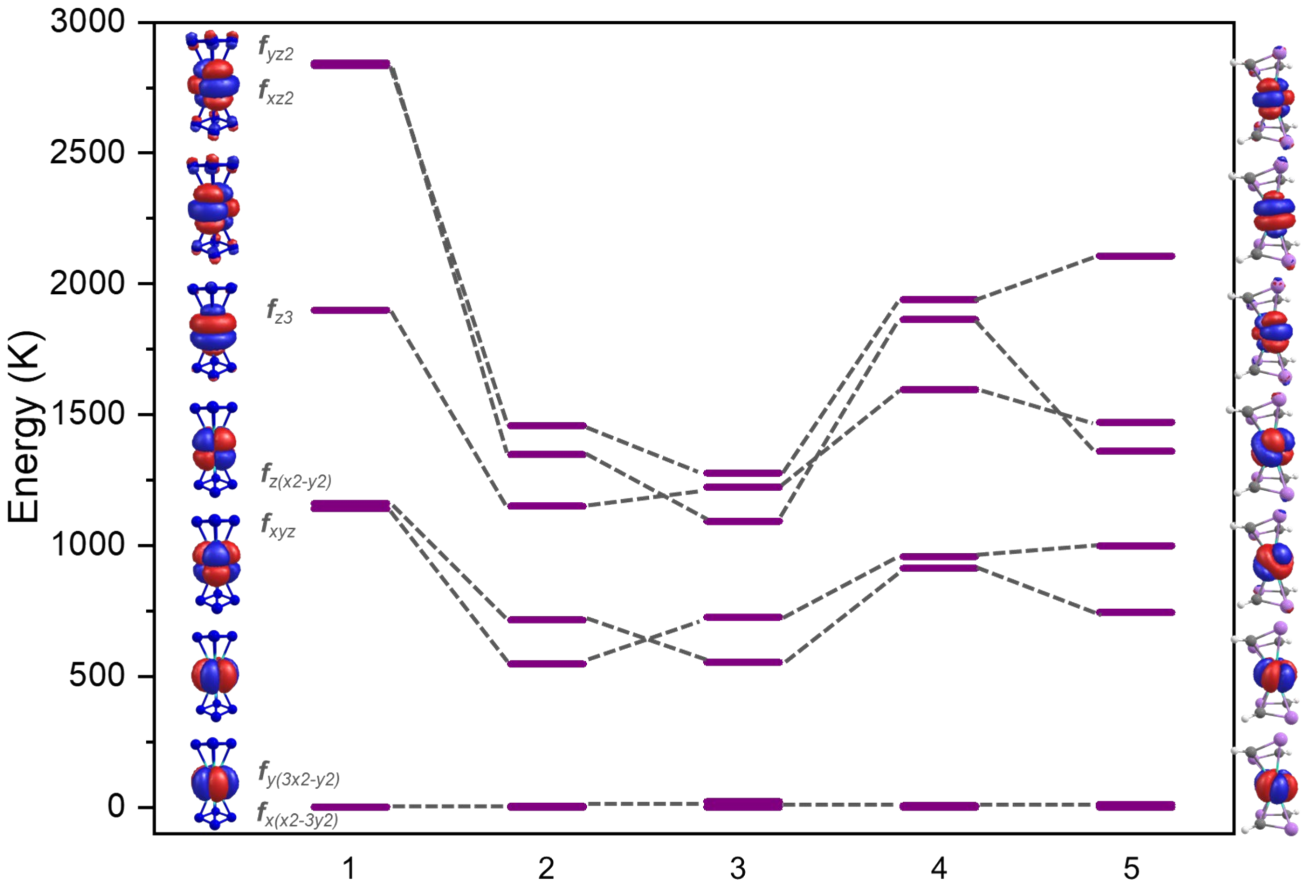


Figure S6: AILFT computed splitting pattern of 4*f* orbitals in complexes **1-5** at NEVPT2 level of theory.

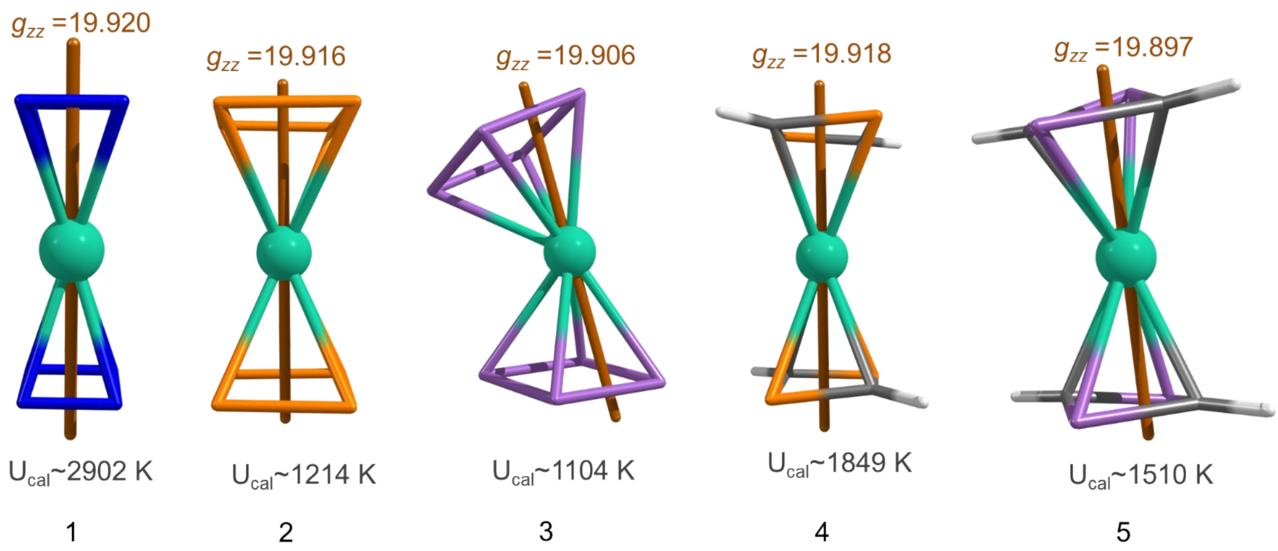


Figure S7: SINGLE_ANISO computed g-tensor orientation in complexes **1-5**

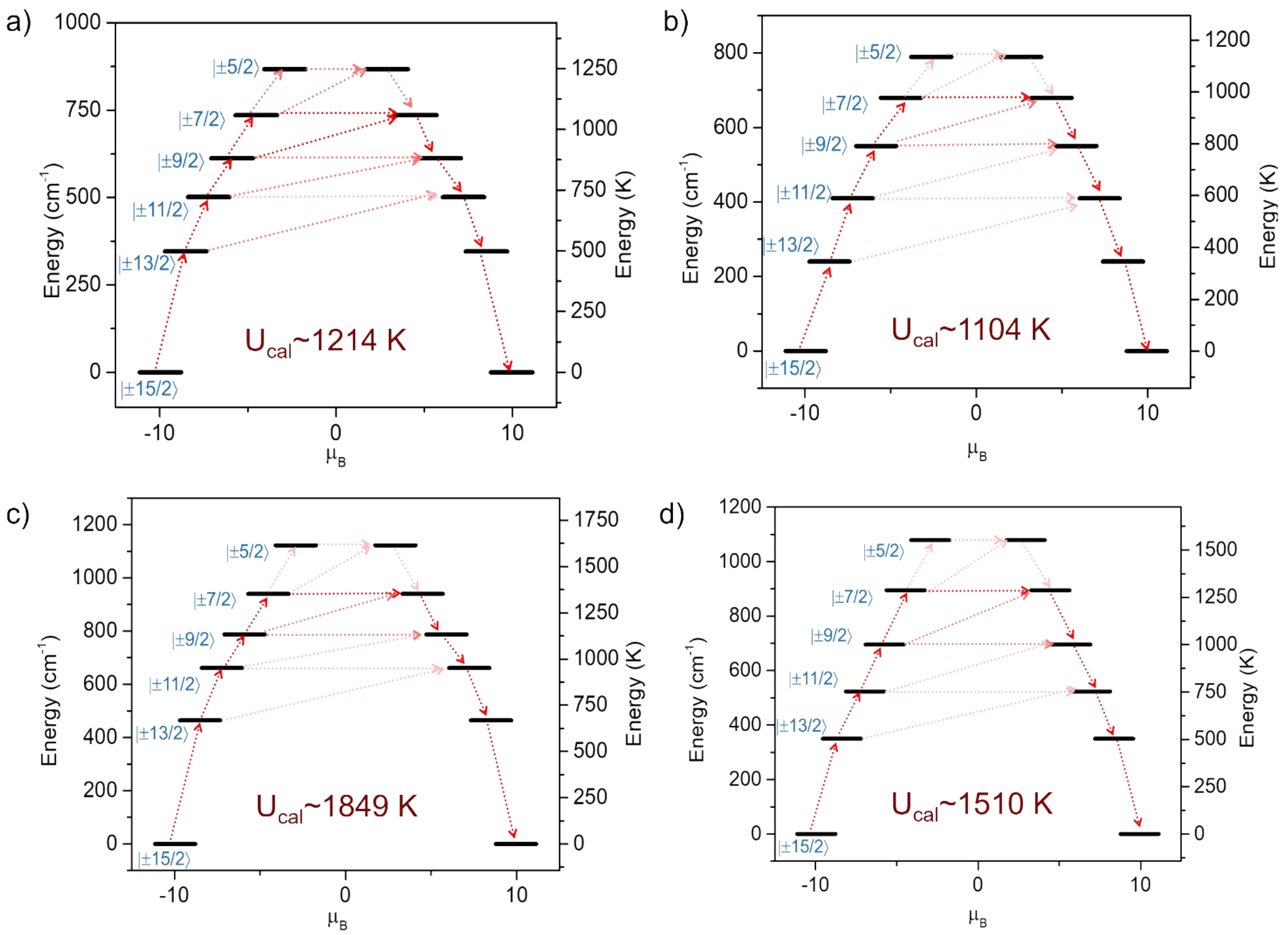


Figure S8: SINGLE_ANISO computed blockade barrier for the complexes (a) **2**, (b) **3**, (c) **4**, (d) **5**.

Table S12: SINGLE_ANISO computed barrier height (U_{cal}), theoretically calculated U_{eff} and the three majorly contributed KDs.

Complexes	U_{cal} (K)	U_{eff} (K)	% contribution from KDs
1	2270.1	2416.0	40% KD5 + 39% KD6 + 30% KD8
2	1213.9	1355.0	36% KD6 + 26% KD7 + 27% KD8
3	1104.4	1175.0	19% KD5 + 31% KD6 + 27% KD8
4	1849.3	1766.0	53% KD5 + 32% KD6 + 26% KD8
5	1509.9	1366.0	21% KD5 + 18% KD6 + 16% KD7

Table S13: SINGLE_ANISO computed the properties of the two lowest Kramers' doublets of the $^6H_{15/2}$ multiplet in complexes **1-5** in the absence of spin-orbital coupling (SOC-off) for N, P, and As atoms.

	KD	E / K	g_{xx}	g_{yy}	g_{zz}	θ	m_J	U_{cal} /K
1	KD1	0.0	0.000	0.000	19.776	-	$\|\pm15/2\rangle$	2805.1
	KD2	1137.7	0.011	0.011	16.919	0.9	$\|\pm13/2\rangle$	
2	KD1	0	0.000	0.000	19.768	-	$\|\pm15/2\rangle$	1032.8
	KD2	473.5	0.001	0.001	17.034	0.0	$\|\pm13/2\rangle$	
3	KD1	0.0	0.000	0.000	19.757	-	$\|\pm15/2\rangle$	953.9
	KD2	334.2	0.000	0.000	17.066	0.1	$\|\pm13/2\rangle$	
4	KD1	0.0	0.000	0.000	19.771	-	$\|\pm15/2\rangle$	1833.5
	KD2	643.8	0.007	0.007	17.022	1.7	$\|\pm13/2\rangle$	
5	KD1	0	0.000	0.000	19.746	-	$\|\pm15/2\rangle$	1514.8
	KD2	490.0	0.018	0.025	16.749	0.2	$\|\pm13/2\rangle$	

Table S14: NEVPT2 computed 21 roots of sextet states along with eight low-lying spin-orbit states for complex **1**. All the values are reported here in cm^{-1}.

1		
Term	**Spin-free states**	**Spin-orbit states**
^{6}H	0.0 0.1 1009.6 1009.6 1432.5 1486.5	0.0 775.6 1055.2 1168.2 1355.83 1621.47

	1488.9	1897.36
	1511.9	2073.31
	2144.9	
	2148.5	
	2276.3	
^{6}F	7194.2	
	7198.1	
	7458.4	
	7492.4	
	7822.0	
	7851.2	
	7851.4	
^{6}P	28635.1	
	30800.2	
	30810.4	

Table S15: NEVPT2 computed 21 roots of sextet states along with eight low-lying spin-orbit states for complexes **2** and **3**. All the values are reported herein cm^{-1}.

2			**3**	
Spin-orbit states	**Spin-free states**	**Term**	**Spin-free states**	**Spin-orbit states**
0.0	0.0	^{6}H	0.0	0.0
345.7	0.3		1.5	240.4
501.5	572.7		377.6	409.7
612.6	576.3		386.9	550.1
735.5	578.6		534.8	679.6
867.1	586.4		588.6	789.2
999.4	724.4		709.9	890.4
1082.3	871.9		831.6	928.7
	1056.2		931.7	
	1105.2		942.1	
	1175.1		979.4	
	6568.1	^{6}F	6474.9	
	6601.4		6537.8	
	6660.0		6554.2	
	6719.9		6562.2	
	6748.5		6636.2	
	6871.1		6746.3	
	6872.2		6758.6	
	28531.5	^{6}P	28438.0	
	29579.3		29381.4	
	29679.0		29498.0	

Table S16: NEVPT2 computed 21 roots of sextet states along with eight low-lying spin-orbit states for complexes **4** and **5**. All the values are reported herein cm^{-1}.

4			**5**	
Spin-orbit states	**Spin-free states**	**Term**	**Spin-free states**	**Spin-orbit states**
0.0	0.0	^{6}**H**	0.0	0.0
261.4	0.0		0.5	350.3
488.7	420.9		527.6	523.4
681.9	420.9		561.8	695.3
840.4	735.3		602.3	894.4
972.8	735.4		667.5	1078.5
1061.4	959.6		997.7	1229.3
1101.7	965.3		1151.7	1330.3
	1099.9		1329.6	
	1103.6		1358.7	
	1141.0		1432.6	
	6717.1	^{6}**F**	6552.2	
	6758.0		6781.8	
	6760.4		6828.9	
	6879.1		6852.5	
	6883.1		6901.8	
	7063.8		7059.8	
	7063.8		7066.6	
	29099.4	^{6}**P**	28427.5	
	30447.9		29583.5	
	30457.0		30003.1	

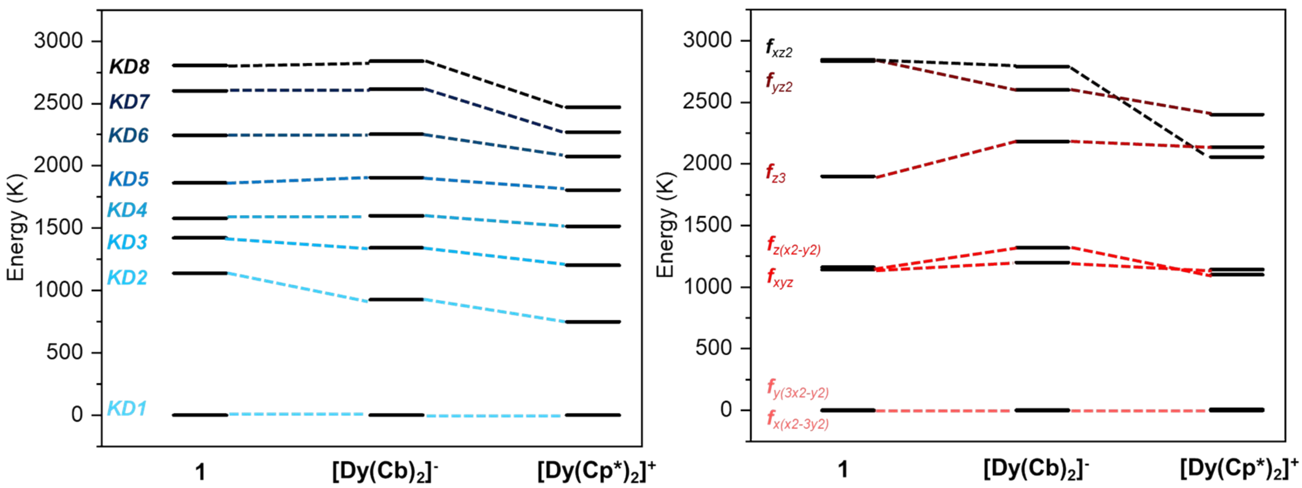


Figure S9: NEVPT2 computed eight low-lying KDs (left) and AILFT computed splitting pattern of 4*f* orbitals (right) for complexes **1**, $[Dy(Cb)_2]^-$, $[Dy(Cp^*)_2]^+$.

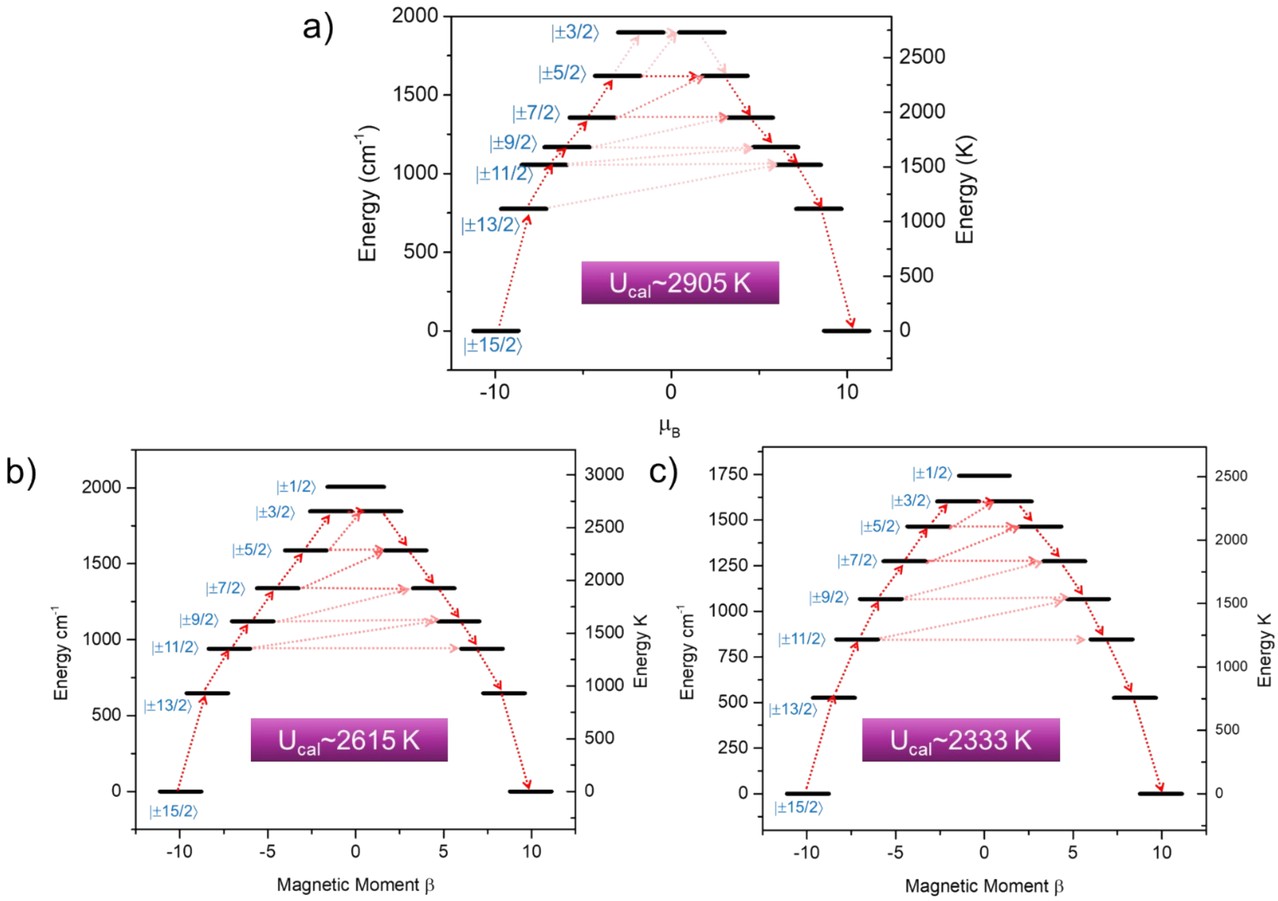


Figure S10: NEVPT2 computed blockade barrier for the reversal of magnetization of complexes **1** (a), $[Dy(Cb)_2]^-$ (b), $[Dy(Cp^*)_2]^+$ (c).

Table S17: NEVPT2 computed 224 roots of quartet for **1**. All the values are reported herein cm^{-1}.

1				
Spin-free State				
24055.3	27937.1	33822.0	53170.3	70800.9
24058.4	28881.1	33823.8	53399.4	71235.2
24316.5	28881.1	33926.4	53462.5	71235.2
24316.5	29674.5	33926.7	53463.3	71284.2
24456.0	29674.5	34134.1	53970.4	71285.5
24488.2	30013.8	34137.1	53973.4	71479.6
24656.6	30014.0	34867.3	54142.1	71504.6
24692.8	30108.9	34880.2	54150.0	72282.2
24696.6	30109.3	35109.7	54176.4	72621.2
24719.1	30270.4	35183.4	54458.9	72625.0
25098.0	30270.4	35204.0	54459.2	75078.5
25107.3	30398.0	35309.2	54779.4	75698.4
25113.3	30406.8	35311.6	54779.4	75705.4
25117.1	30503.3	35971.1	58331.8	77324.5
25207.6	30523.1	36275.1	58334.6	77331.5
25282.3	30592.2	36287.3	58340.3	80204.2
25335.3	30593.5	36313.0	58376.1	80242.0
25428.5	30694.1	36313.2	58423.5	80254.9
25430.1	30694.9	40610.8	58481.8	80255.0
25431.8	30748.1	40619.0	58482.9	80308.3
25436.5	30767.9	41566.7	58777.5	80404.3
25439.1	30835.4	41640.5	58778.2	80405.4
25612.8	30972.4	41697.0	59214.5	81188.1
25638.1	32197.1	42013.8	59214.5	81188.1
25638.1	32263.6	42014.0	59830.4	82286.5
25773.0	32264.2	43114.0	59830.6	82286.7
25845.4	32448.6	43186.7	59970.7	82378.3
25849.5	32465.9	43191.2	59970.7	82378.3
25889.3	32504.3	43434.1	60710.2	87876.0
25889.8	32504.8	43503.3	60720.7	87886.4
26156.6	32643.6	43702.1	62832.3	88547.9
26195.1	32643.7	43702.5	65361.0	88996.0
26344.2	32657.3	43886.6	65410.9	89180.5
26612.4	32657.3	43887.3	66956.2	90072.7
26613.3	32738.9	44045.2	67376.8	90072.8
26640.7	32739.4	44045.2	67385.3	94640.6
27233.3	32777.3	44824.9	70446.3	95244.7
27370.6	32777.3	44825.5	70570.6	95251.8
27521.8	32817.7	52082.8	70593.2	95772.5
27619.3	32817.7	52083.1	70614.7	95860.7
27638.3	33251.1	52791.7	70615.0	96477.0
27638.4	33252.4	52792.2	70661.1	96477.3
27643.6	33559.1	52879.3	70661.6	96537.4
27654.2	33643.4	52946.5	70722.3	96537.7
27929.6	33643.4	53166.8	70800.8	

Table S18: NEVPT2 computed 224 roots of quartet for **2**. All the values are reported herein cm^{-1}.

2				
Spin-free State				
24037.7	27336.2	33065.5	52732.7	70297.1
24051.4	27637.0	33075.4	52777.1	70380.6
24051.6	27637.0	33100.8	52811.7	70380.7
24208.3	29413.9	33109.3	52814.9	70393.8
24208.6	29413.9	33133.6	52922.2	70394.5
24306.9	29566.4	33190.1	52959.4	70672.8
24313.7	29567.1	33866.0	53088.6	70728.1
24318.0	29596.2	33928.2	53117.7	71101.6
24360.8	29601.2	34182.9	53199.4	71160.2
24383.6	29611.1	34836.9	53270.9	71193.0
24401.9	29613.0	34881.6	53277.6	74807.4
24466.1	29670.6	34906.8	53494.9	75081.0
24498.3	29672.3	34928.4	53534.4	75146.2
24539.1	29695.1	35043.3	57964.2	75949.3
24549.5	29730.6	35266.8	57965.1	75958.8
24611.2	29805.2	35268.0	58004.0	79880.2
24620.8	29815.5	35364.0	58019.1	79889.8
24625.0	29844.6	35379.0	58025.3	79914.5
24646.9	30038.4	40399.1	58081.1	79924.3
24652.7	30038.5	40467.3	58084.2	79987.3
24738.8	30040.8	40689.4	58216.3	80068.5
24795.8	30093.3	40758.6	58216.3	80077.4
24815.8	30130.5	40908.9	58419.2	80383.5
24837.5	31716.9	41044.5	58419.2	80385.1
24846.3	31728.6	41047.2	58662.8	80809.6
24888.0	31738.8	42748.0	58662.9	80809.7
24929.2	31764.6	42772.3	58777.3	81039.6
25131.0	31774.7	42809.4	58777.3	81039.7
25146.1	31774.7	42891.7	60406.9	87896.2
25156.0	31792.9	42910.2	60508.9	87986.9
25262.9	31795.2	43022.5	61583.5	88098.5
25366.1	31795.2	43025.0	65298.1	88417.3
25592.8	31826.6	43137.9	65323.4	88473.5
25799.1	31827.9	43140.1	66259.2	89169.7
26002.5	31838.5	43261.9	66321.8	89173.6
26046.0	31838.8	43262.0	66338.4	94296.0
27048.9	31857.6	43559.9	69066.2	94475.4
27054.3	31859.3	43559.9	70108.5	94527.9
27059.7	31865.3	52013.7	70109.0	94769.2
27078.2	31865.4	52015.3	70110.7	94802.0
27113.6	32842.4	52453.3	70121.9	95039.5
27119.7	32843.9	52568.9	70126.5	95040.4
27135.3	32912.6	52573.0	70200.5	95200.0
27136.6	32912.7	52629.3	70203.0	95200.2
27336.2	33030.3	52640.5	70296.5	

Table S19: NEVPT2 computed 224 roots of quartet for **3**. All the values are reported herein cm^{-1}.

3				
Spin-free State				
23619.3	27297.2	32940.4	52570.1	70168.5
23953.1	27456.4	32961.6	52613.6	70176.7
23953.3	27456.4	32966.1	52711.1	70177.7
23965.7	29376.2	32985.6	52713.1	70215.0
24116.2	29376.4	33015.4	52746.1	70215.2
24117.7	29488.2	33023.0	52775.8	70530.7
24187.3	29489.4	33745.3	52881.6	70564.4
24196.0	29502.8	33797.2	52941.7	70857.0
24199.4	29509.3	34046.7	53022.2	70934.9
24244.6	29516.4	34768.2	53042.8	70946.8
24272.6	29524.5	34829.2	53047.5	74665.2
24394.7	29568.7	34842.7	53290.4	74915.3
24407.6	29583.8	34859.6	53364.2	74974.8
24422.9	29617.4	34885.1	57822.9	75695.8
24432.7	29637.8	35060.5	57822.9	75703.0
24452.3	29651.7	35087.6	57887.6	79702.0
24471.1	29678.4	35249.7	57909.2	79705.4
24471.4	29681.1	35264.4	57911.1	79793.9
24536.2	29933.7	40367.8	57978.3	79812.7
24577.1	29939.3	40463.8	57979.1	79852.4
24580.7	29940.5	40494.7	58093.4	79950.4
24682.4	29989.8	40599.7	58094.2	79970.8
24693.9	30001.0	40739.6	58249.4	80200.3
24703.0	31649.8	40899.5	58249.8	80202.2
24759.5	31650.6	40928.9	58438.8	80511.2
24888.1	31670.6	42685.0	58438.8	80512.1
24919.0	31671.8	42704.5	58606.1	80815.1
25129.3	31672.3	42718.5	58606.1	80815.1
25237.0	31672.4	42770.7	60299.5	87814.9
25300.0	31697.2	42798.0	60385.6	87866.2
25460.1	31704.1	42888.0	61362.0	87940.3
25545.8	31704.5	42888.2	65197.1	88187.8
25598.9	31704.9	43010.1	65223.2	88259.9
25854.9	31707.5	43011.8	66050.8	88910.2
25856.1	31716.7	43156.7	66132.2	88914.3
26092.0	31717.6	43156.7	66159.5	94163.6
26556.0	31731.1	43367.8	68941.3	94276.9
26742.6	31732.5	43367.8	69894.7	94291.0
26939.0	31732.9	51931.5	69931.9	94503.2
27050.0	31733.8	51932.3	69939.2	94538.3
27141.8	32782.6	52378.1	69949.8	94789.0
27148.4	32784.0	52494.9	69990.1	94793.9
27200.1	32821.5	52527.2	70053.8	94923.7
27203.6	32821.8	52535.7	70058.4	94924.2
27297.1	32933.6	52551.5	70145.1	

Table S20: NEVPT2 computed 224 roots of quartet for **4**. All the values are reported herein cm^{-1}.

4				
Spin-free State				
24111.6	27680.9	33284.8	52779.5	70381.3
24111.6	27953.3	33313.7	52792.1	70468.7
24315.8	27953.3	33344.3	53081.3	70544.8
24342.8	29546.4	33371.0	53082.4	70633.7
24368.0	29546.5	33382.8	53242.8	70633.9
24368.6	29774.8	33418.9	53244.1	70935.8
24411.2	29774.9	34210.9	53383.0	70968.0
24452.1	29782.3	34224.5	53442.3	71439.0
24453.1	29784.9	34680.6	53489.3	71539.2
24453.2	29786.2	34823.0	53493.1	71574.3
24670.1	29787.2	35079.3	53622.0	74788.9
24676.2	29886.0	35093.7	53834.4	75167.0
24699.6	29887.1	35106.6	53985.6	75220.1
24833.9	29944.5	35151.3	57999.5	76347.6
24834.6	29962.9	35340.5	58002.6	76349.8
24961.2	29974.7	35432.6	58051.2	79846.1
24976.5	30075.9	35734.2	58082.3	79859.6
25018.5	30081.4	35736.7	58093.5	79940.7
25045.4	30193.0	40486.5	58188.0	79985.4
25102.6	30230.0	40665.5	58189.1	80005.9
25131.8	30276.4	40761.0	58365.0	80201.1
25132.5	30282.2	41004.6	58365.1	80203.5
25161.2	30343.5	41064.1	58607.0	80575.6
25262.7	31947.7	41358.0	58607.1	80575.8
25387.6	31949.0	41363.2	58927.8	81089.3
25445.5	32012.7	42846.9	58927.8	81089.7
25461.7	32015.8	42880.1	59217.0	81529.4
25513.5	32020.2	42902.7	59217.0	81529.4
25561.2	32020.2	43008.4	60411.6	87891.0
25700.0	32028.2	43014.6	60486.3	87943.7
25709.1	32042.9	43170.0	61981.7	88035.2
25763.0	32044.1	43171.4	65246.6	88460.0
25822.1	32069.4	43354.5	65249.4	88482.0
25904.9	32069.9	43354.9	66529.4	89422.5
25914.1	32081.2	43580.8	66559.8	89424.0
25919.8	32081.6	43580.9	66618.8	94371.8
26064.9	32134.7	43911.9	69533.6	94539.7
26735.5	32134.7	43912.0	70183.1	94619.4
26769.4	32142.4	51945.1	70188.4	94975.0
26852.2	32142.4	51945.3	70189.2	94980.5
27305.3	33039.2	52586.4	70211.5	95448.0
27307.6	33039.5	52643.9	70219.7	95451.9
27488.6	33089.8	52689.4	70281.7	95518.8
27491.8	33090.5	52717.4	70281.8	95518.9
27680.9	33256.0	52743.1	70379.0	

Table S21: NEVPT2 computed 224 roots of quartet for **5**. All the values are reported herein cm^{-1}.

5				
Spin-free State				
24069.9	27453.3	33139.2	52770.3	70293.9
24070.1	27893.1	33180.3	52774.4	70365.4
24271.4	27893.1	33223.7	52887.8	70384.5
24278.1	29438.1	33286.3	52897.4	70384.6
24383.0	29438.1	33302.0	53074.2	70415.8
24407.8	29610.2	33326.9	53087.2	70723.5
24415.2	29610.2	33903.0	53205.4	70748.7
24438.1	29617.2	34255.5	53312.6	71260.3
24511.9	29618.1	34390.3	53325.1	71274.3
24524.5	29774.4	34817.6	53336.6	71421.4
24548.3	29774.7	34841.6	53402.4	74665.3
24620.0	29786.3	34872.7	53723.4	74944.7
24707.5	29789.1	34953.7	53753.4	75191.9
24723.2	29845.1	35127.8	57833.0	76100.7
24731.3	29863.7	35416.3	57836.5	76104.5
24734.3	29913.7	35422.7	57973.8	79678.1
24781.1	29968.1	35539.4	57989.7	79696.2
24789.3	29977.6	35556.7	58027.1	79838.1
24789.7	30069.9	40192.3	58078.0	79887.1
24956.2	30120.7	40705.6	58087.4	79957.4
24977.8	30120.7	40774.1	58237.4	80024.7
25020.3	30187.3	40788.7	58238.4	80038.2
25058.8	30298.9	40984.5	58479.9	80391.7
25082.3	31772.7	41208.5	58480.0	80394.3
25087.8	31773.0	41210.1	58807.5	80966.8
25135.9	31873.8	42715.3	58807.5	80966.8
25153.5	31875.4	42716.9	58952.7	81217.9
25249.3	31875.4	42857.3	58953.9	81218.0
25312.8	31882.9	42899.9	60193.2	87560.7
25359.3	31912.4	43002.5	60557.1	87901.9
25369.9	31928.6	43078.7	61752.0	87906.4
25375.0	31929.7	43124.6	65164.7	88356.5
25542.4	31948.6	43207.2	65168.5	88455.0
25543.1	31957.5	43219.7	66242.0	89217.3
26009.1	31960.9	43375.0	66404.9	89249.9
26485.2	31966.7	43375.4	66542.6	94175.3
26550.0	32032.7	43773.7	69288.6	94340.6
26578.9	32033.1	43773.8	70057.3	94543.6
26595.8	32033.5	51897.0	70060.9	94751.0
26727.2	32033.8	51897.3	70064.9	94845.0
27012.2	32908.4	52432.4	70064.9	95133.1
27261.1	32911.9	52434.4	70091.9	95149.3
27264.9	32955.8	52561.3	70167.4	95298.0
27324.1	32957.2	52567.3	70171.8	95298.6
27451.7	33123.9	52617.4	70291.8	

Table S22: DFT-optimized geometry coordinates.

1			
Dy	0.000000000000	0.000000000000	0.000000000000
N	0.237478000000	0.955323000000	2.183555000000
N	-0.953451000000	0.238222000000	2.182404000000
N	0.956073000000	-0.238222000000	2.180903000000
N	-0.235322000000	-0.954905000000	2.179571000000
N	-0.955825000000	0.233820000000	-2.181058000000
N	-0.231760000000	-0.956434000000	-2.183666000000
N	0.232215000000	0.955974000000	-2.179673000000
N	0.955825000000	-0.233820000000	-2.182365000000

2			
Dy	0.000000000000	0.000000000000	0.000000000000
P	1.364347000000	0.772382000000	-2.470035000000
P	0.759113000000	-1.343829000000	-2.439751000000
P	-1.364347000000	-0.772382000000	-2.470197000000
P	-0.759458000000	1.343641000000	-2.439369000000
P	-1.284933000000	-0.894153000000	2.470294000000
P	-0.878738000000	1.267074000000	2.440409000000
P	1.290245000000	0.894153000000	2.468615000000
P	0.884003000000	-1.267670000000	2.438511000000

3			
Dy	0.000000000000	0.000000000000	0.000000000000
As	-0.019870000000	-1.699453000000	-2.410430000000
As	-1.719218000000	0.017781000000	-2.442727000000
As	0.015488000000	1.698905000000	-2.416102000000
As	1.723600000000	-0.017233000000	-2.418255000000
As	1.231435000000	1.699614000000	2.072649000000
As	2.723129000000	0.009138000000	1.184388000000
As	1.251393000000	-1.698916000000	2.065738000000
As	-0.214755000000	-0.009835000000	2.979493000000

4			
Dy	0.000000000000	0.000000000000	0.000000000000
C	-1.180124000000	0.074436000000	-2.356261000000
C	0.042746000000	-1.167379000000	2.335341000000
H	-2.272590000000	0.142828000000	-2.441060000000
H	-0.021372000000	-2.263532000000	2.393825000000
P	-0.085761000000	-1.359406000000	-2.468836000000
P	-1.256371000000	0.082915000000	2.526708000000
C	1.180036000000	-0.074464000000	-2.354790000000
H	2.272872000000	-0.143390000000	-2.430841000000
P	0.085848000000	1.359434000000	-2.469120000000
C	0.183221000000	1.167450000000	2.328749000000
H	0.251382000000	2.263713000000	2.379573000000

P	1.495894000000	-0.082985000000	2.391714000000

5			
Dy	0.000000000000	0.000000000000	0.000000000000
C	-0.028061000000	-1.221426000000	-2.286059000000
C	0.968759000000	1.221788000000	2.069668000000
H	-0.055063000000	-2.320602000000	-2.341122000000
H	0.997220000000	2.321369000000	2.114478000000
As	1.479037000000	-0.034525000000	-2.455145000000
As	2.374261000000	-0.010756000000	1.606113000000
C	0.029490000000	1.221246000000	-2.285961000000
H	0.054281000000	2.320604000000	-2.337490000000
As	-1.480466000000	0.034705000000	-2.442105000000
C	0.954021000000	-1.221666000000	2.078558000000
H	0.968829000000	-2.321186000000	2.131021000000
As	-0.317266000000	0.010634000000	2.838437000000

EDA Input File

```
Task SinglePoint
System
   Atoms
      coordinates
   End
   Charge -1.0

Engine ADF
   Basis
      Type TZ2P
      Core None
   End
   SpinPolarization 5.0
   Fragments
      Region_1 =/path/adf.rkf
      Region_2 =/path/adf.rkf
   End

   Save TAPE15
   Print ETSLOWDIN-Unrestricted
   Print NOCVHIRSHFELD
   XC
      Hybrid PBE0
      DISPERSION GRIMME3 BJDAMP
   End
   Symmetry NOSYM
   Unrestricted Yes
   BeckeGrid
      Quality Good
```

```
    End
    LOCORB
    END
    NumericalQuality Good
    FullFock Yes
    AOMat2File Yes
        SCF
Iterations 800
End
UnrestrictedFragments Yes
    ETSNOCV
        Enabled Yes
    End
EndEngine
eor
```

CASSCF Input File

```
!DKH2 DKH-def2-SVP slowconv tightscf autoaux

%pal nprocs 40
end

%Maxcore 6000

%basis newgto Dy "SARC-DKH2-TZVP"
end
end

%method
SpecialGridAtoms 66
SpecialGridIntAcc 9
end

%casscf
nel 9
norb 7
mult 6,4
nroots 21,224
actorbs forbs
nevpt2 true
maxiter 100
ci
nguessmat 8000
maxiter 100
end

rel
dosoc true
gtensor true
```

```
printlevel 3
NDoubGTensor 8
domagnetization true
dosusceptibility true

SUSTempMIN 2.0
SUSTempMAX 300.0
SUSNPoints 100

MAGTemperatureMIN 2.0
MAGTemperatureMAX 5.0
MAGTemperatureNPoints 4

MAGFieldMIN 0.0
MAGFieldMAX 70000.0
MAGNpoints 15

end

ANISO
doaniso true
MLTP 2,2,2,2,2,2,2,2
TINT 0, 300, 100
HINT 0, 7.0, 10
TMAG 2.0, 3.0, 5.0
CRYS_element "Dy"
CRYS_charge 3
PLOT true
UBAR true
end
end

*xyz -1 6
Coord
*
```