Supplementary Information (SI) for Materials Chemistry Frontiers.

Accelerating Spin-Flip Process of Multi-Resonance Emitter via Advanced Nitrogen Group Heavy Atom Strategy

Weibo Cui[a], Yexuan Pu[a], Linjie Li[a], Lixiao Guo[a], Pingping Zheng[a], Yun Geng*[b] and Chenglong Li*[a]

[a] W. Cui, Y. Pu, L. Li, L. Guo, P. Zheng, C. Li
State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, P. R. China.
E-mail: chenglongli@jlu.edu.cn (C. Li)
[b] Y. Geng
School of Physics, Northeast Normal University, Changchun 130024, P. R. China.
E-mail: gengy575@nenu.edu.cn (Y. Geng)

Content

13. Table S8 Singlet-triplet energy gaps $\Delta E_{S\text{-}T}$ (eV), spin-orbit coupling SOC (cm^{-1}), and reverse intersystem crossing rates k_{RISC} (s^{-1}) for the studied molecules and the corresponding oxygen group heavy atom substituted molecules (1-Z, Z=O/S/Se).

14. Table S9 Absorption properties of the studied molecules, including maximum absorption peaks λ_{abs} (nm), oscillator strength *f*, vertical excitation energies E_{vt} (eV), transition moments μ (D), and corresponding transition nature by TPSSh/6-31G(d).

15. Table S10 Fluorescence properties of the studied molecules, including fluorescence emission wavelengths λ_{emi} (nm), oscillator strength *f*, vertical excitation energies E_{vt} (eV), transition moments μ (D), and corresponding transition nature by TPSSh/6-31G(d).

16. Table S11 Cartesian coordinates of all studied compounds at optimized S_0 geometry.

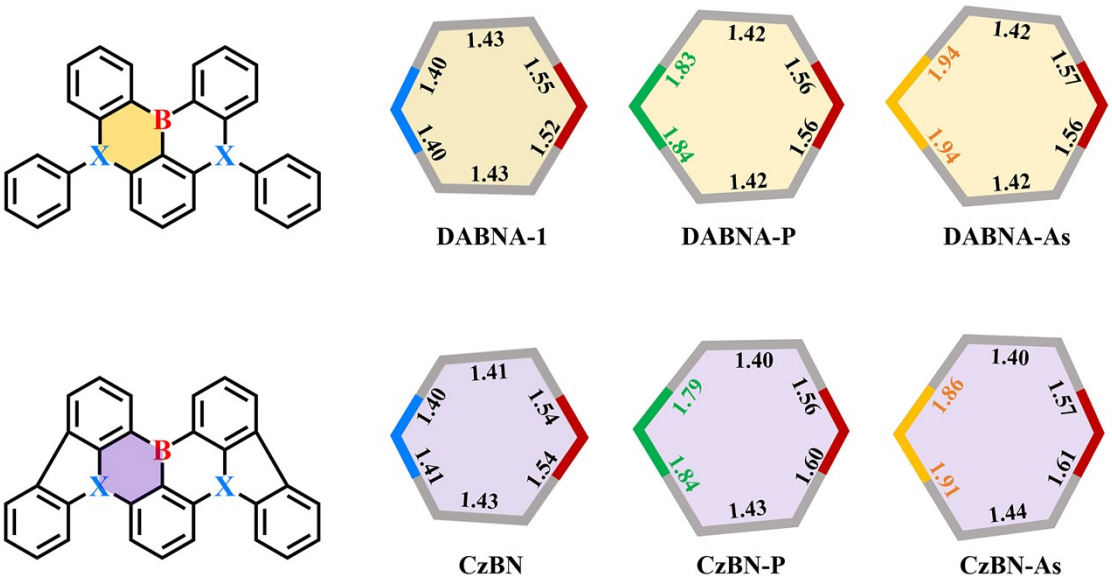


Figure S1 Bond lengths (in Å) of the studied molecules in the S_0 state.

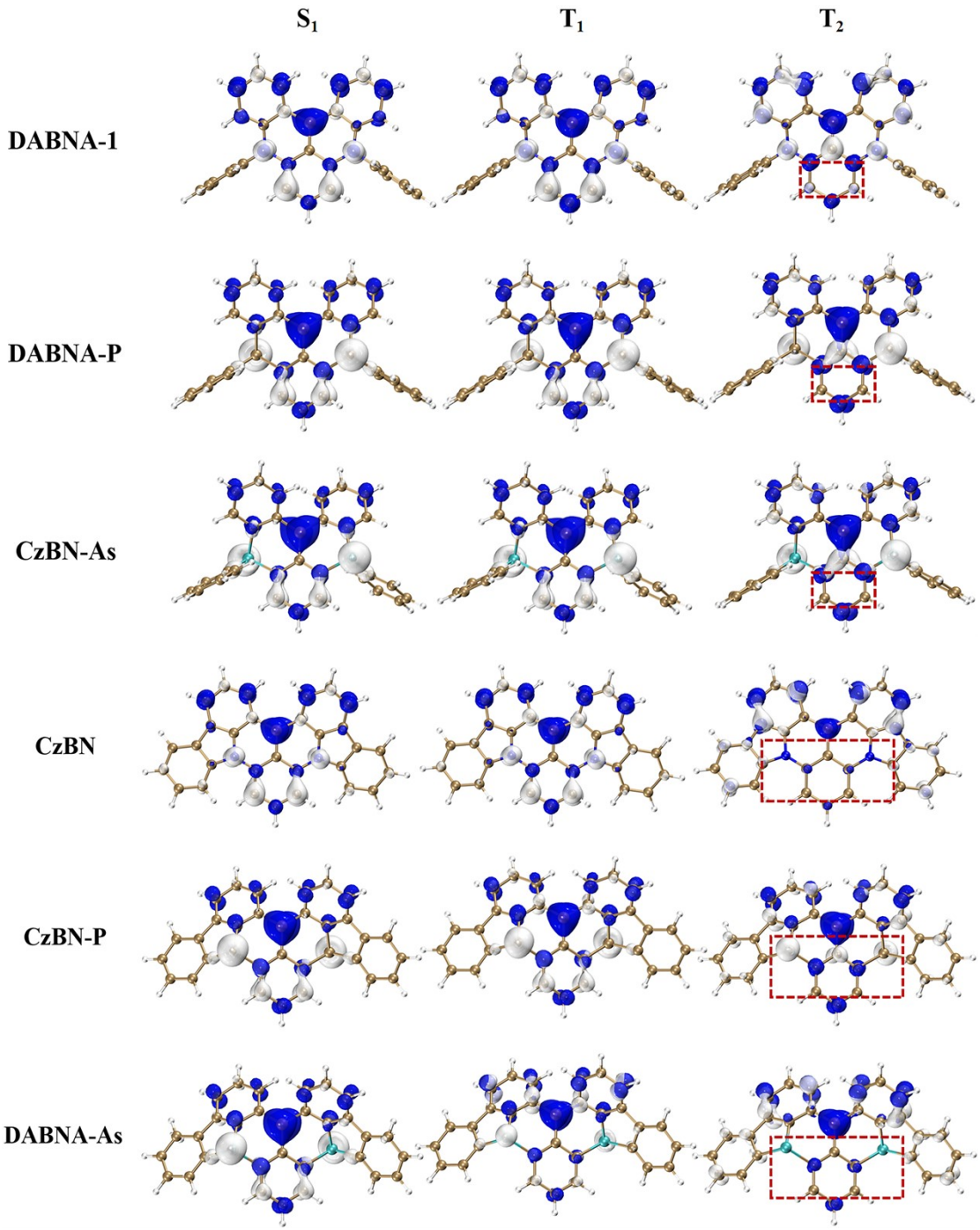


Figure S2 Contour surfaces of hole-electron distribution of the S_1, T_1, and T_2 states of the studied molecules (white represents the hole part and blue represents the electron part).

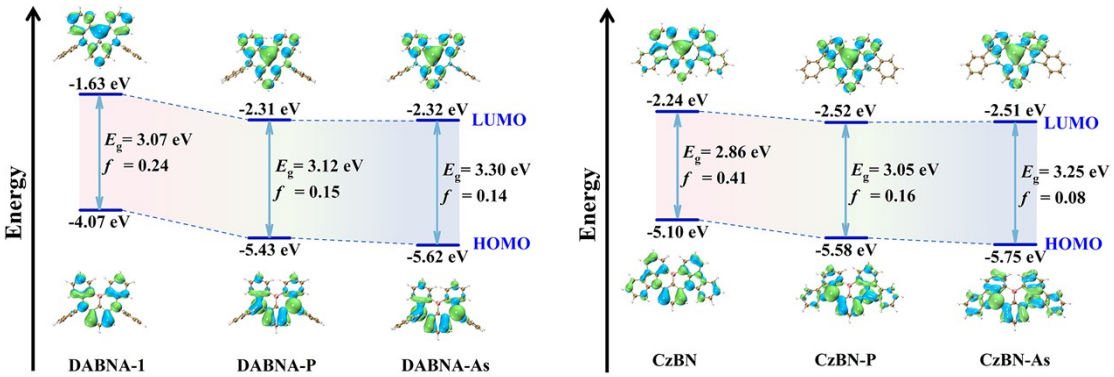


Figure S3 Frontier molecular orbital energy levels and contour surfaces (Isosurface = 0.03) for the S_0 states of the studied molecules.

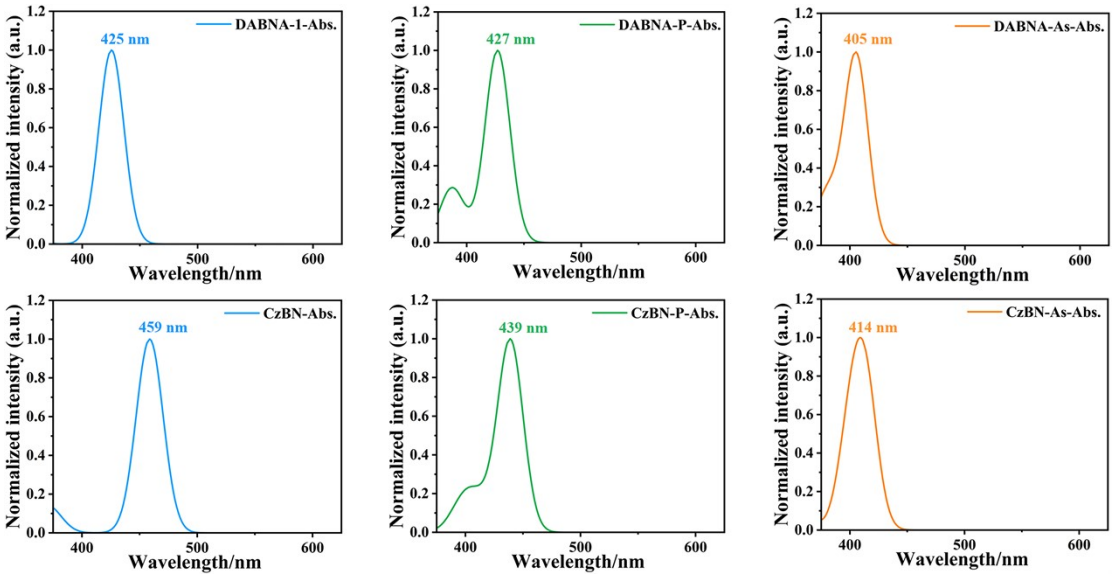


Figure S4 Absorption spectra of the studied molecules.

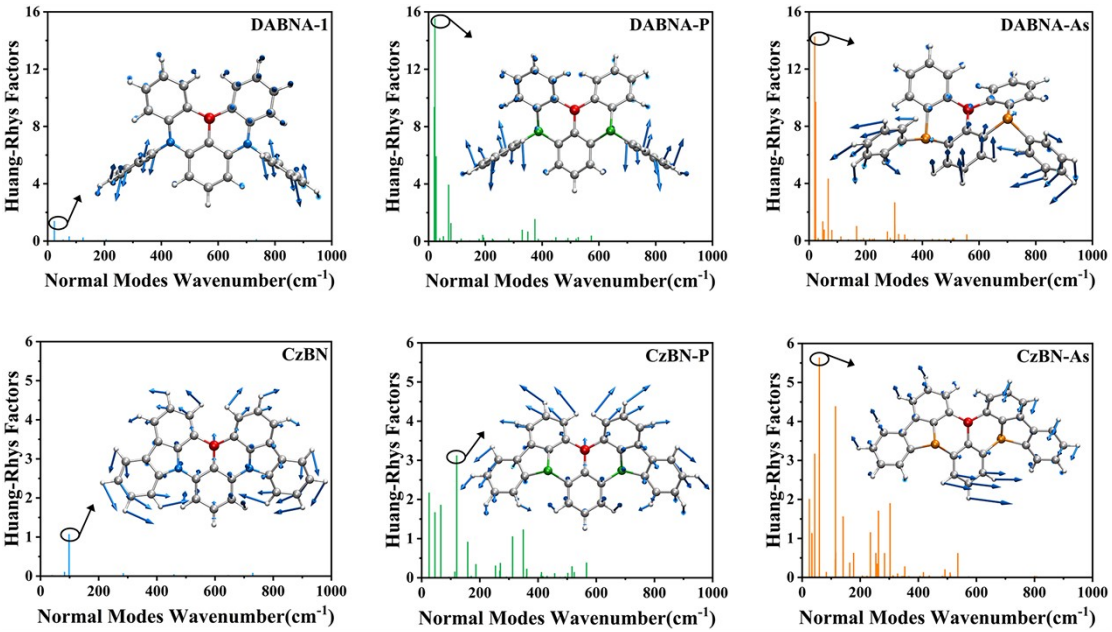


Figure S5 Huang-Rhys Factors and crucial displacement vectors for the normal modes with large HR in the low-frequency regime (<500 cm^{-1}) for the studied molecules.

Table S1 Maximum absorption peak λ_{abs} (nm), maximum emission peak λ_{emi} (nm), and corresponding oscillator strengths f of experimental molecules **DABNA-1** and **CzBN**, using different functionals and 6-31G(d) basis set.

Mol.	Functional	f	λ_{abs}/nm	f	λ_{emi}/nm
DABNA-1	**TPSSh**	**0.24**	**425.32**	**0.23**	**462.15**
	O3LYP	0.24	422.70	0.23	458.45
	B3LYP	0.27	403.56	0.29	433.16
	M06-2X	0.41	353.48	0.50	372.18
	ωB97XD (ω=0.1371) [b)]	0.37	367.89	0.30	386.11
	Experimental date[a)]	--	**437**	--	**462**
CzBN	**TPSSh**	**0.41**	**458.75**	**0.46**	**490.85**
	O3LYP	0.40	456.96	0.46	488.30
	B3LYP	0.46	432.87	0.53	459.09
	M06-2X	0.64	372.51	0.80	391.44
	ωB97XD (ω=0.1371)	0.61	387.20	0.54	400.84
	Experimental date[a)]	--	**458**	--	**479**

[a)] Measured in dichloromethane solution (2×10^{-5} M) at 298 k. [b)] The ω value is regulated using the optDFTw program.[1]

Table S2 Comparison of the calculated values (computational methods as described in the text) with the experimental values of the experimental molecules **DABNA-1** and **CzBN**.

Mol.		λ_{abs}/nm	λ_{emi}/nm	ΔE_{ST}/eV	k_{RISC}/s^{-1}	k_f/s^{-1}	FWHM
DABNA-1	Calc.	425	462	0.16	1.14×10^{3}	7.33×10^{7}	30
	Exp.[a)]	437	462	0.15	9.90×10^{3}	9.60×10^{7}	33
CzBN	Calc.	459	491	0.12	2.94×10^{4}	1.28×10^{8}	26
	Exp.[a)]	458	479	0.12	1.69×10^{4}	1.20×10^{8}	30

[a)] Measured in dichloromethane solution (2×10^{-5} M) at 298 k.

Table S3 Dihedral angle values ϕ_1 near the B atom in the ground state and first singlet/triplet excited states of the studied molecules (dihedral angle labels as shown in **Figure 2**).

Mol.	ϕ_1(°)		
	S_0	S_1	T_1
DABNA-1	13	10	10
DABNA-P	30	30	29
DABNA-As	31	31	30
CzBN	11	10	10
CzBN-P	36	32	32

CzBN-As	42	38	36

Table S4 Dihedral angle values ϕ_2 and ϕ_3 near the heavy atoms in the ground state and first singlet/triplet excited states of the studied molecules.

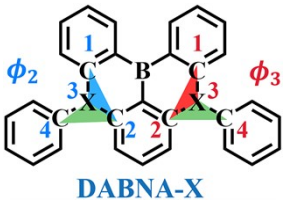
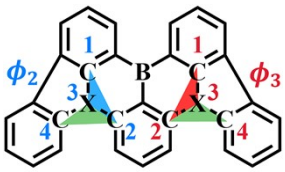
Mol.		ϕ_2(°)			ϕ_3(°)		
		S_0	**S_1**	**T_1**	**S_0**	**S_1**	**T_1**
 DABNA-X	**DABNA-1**	176	177	177	176	177	177
	DABNA-P	106	107	107	106	123	126
	DABNA-As	99	100	100	99	115	116
 CzBN-X	**CzBN**	174	175	175	174	175	175
	CzBN-P	95	110	113	95	95	94
	CzBN-As	88	102	106	88	87	87

Table S5 Singlet-triplet energy gaps $\Delta E_{S\text{-}T}$ (eV), and spin-orbit coupling SOC (cm^{-1}) between S_2 and T_1/T_2 states for the studied molecules.

Mol.	$\Delta E_{S2\text{-}T1}$/eV	$\Delta E_{S2\text{-}T2}$/eV	$\langle T_1 \lvert \hat{H}_{SOC} \rvert S_2 \rangle$/cm^{-1}	$\langle T_2 \lvert \hat{H}_{SOC} \rvert S_2 \rangle$/cm^{-1}
DABNA-1	1.06	0.50	0.11	0.11
DABNA-P	0.53	0.27	0.05	0.23
DABNA-As	0.44	0.28	2.25	1.11
CzBN	0.80	0.43	3.34	1.69
CzBN-P	0.48	0.23	25.76	4.17
CzBN-As	0.36	0.30	16.86	7.19

Table S6 Spin-orbit coupling (SOC) for the S_1-T_1 process of the studied molecules.

Mol.	$\langle S_1 \lvert \hat{H}_{SOC} \rvert T_1 \rangle$/cm^{-1}
DABNA-1	0.03
DABNA-P	0.85
DABNA-As	4.44
CzBN	0.03
CzBN-P	0.80
CzBN-As	2.95

Table S7 Phosphorescence radiative transition rates k_r^T (s^{-1}) and reverse intersystem crossing rates k_{RISC} (s^{-1}) for the studied molecules.

Mol.	$k_{r/s^{-1}}^T$	k_{RISC}/s^{-1}
DABNA-1	0.00×10^0	1.14×10^3
DABNA-P	3.26×10^0	6.49×10^5
DABNA-As	1.23×10^2	2.24×10^7
CzBN	0.00×10^0	2.94×10^4
CzBN-P	3.74×10^0	2.92×10^5
CzBN-As	1.22×10^2	9.13×10^6

Table S8 Singlet-triplet energy gaps $\Delta E_{S\text{-}T}$ (eV), spin-orbit coupling SOC (cm^{-1}), and reverse intersystem crossing rates k_{RISC} (s^{-1}) for the studied molecules and the corresponding oxygen group heavy atom substituted molecules (**1-Z**, Z=O/S/Se).

Mol.	$\Delta E_{S1\text{-}T1}$/eV	$\langle T_1 \lvert \hat{H}_{SOC} \rvert S_1 \rangle$/cm^{-1}	k_{RISC}/s^{-1}
1-O	0.20	0.05	2.26×10^3
1-S	0.16	0.72	2.42×10^5
1-Se	0.15	3.16	1.05×10^7
DABNA-1	0.16	0.03	1.14×10^3
DABNA-P	0.16	1.06	6.49×10^5
DABNA-As	0.17	3.95	2.24×10^7
CzBN	0.12	0.03	2.94×10^4
CzBN-P	0.18	0.83	2.92×10^5
CzBN-As	0.27	2.47	9.13×10^6

Table S9 Absorption properties of the studied molecules, including maximum absorption peaks λ_{abs} (nm), oscillator strength f, vertical excitation energies E_{vt} (eV), transition moments μ (D), and corresponding transition nature by TPSSh/6-31G(d).

Mol.	λ_{abs}/nm	f	E_{vt}/eV	μ/D	Transition nature	
DABNA-1	425.32	0.24	2.92	3.32	$S_0\rightarrow S_1$	H→L（97.82%）
DABNA-P	426.93	0.15	2.90	2.14	$S_0\rightarrow S_1$	H→L（98.57%）
DABNA-As	405.37	0.14	3.06	1.82	$S_0\rightarrow S_1$	H→L（98.68%）
CzBN	458.75	0.41	2.70	6.14	$S_0\rightarrow S_1$	H→L（98.78%）
CzBN-P	438.92	0.16	2.82	2.31	$S_0\rightarrow S_1$	H→L（98.63%）
CzBN-As	413.69	0.08	3.00	1.12	$S_0\rightarrow S_1$	H→L（97.95%）

Table S10 Fluorescence properties of the studied molecules, including fluorescence emission wavelengths λ_{emi} (nm), oscillator strength f, vertical excitation energies E_{vt} (eV), transition moments μ (D), and corresponding transition nature by TPSSh/6-31G(d).

Mol.	λ_{emi}/nm	f	E_{vt}/eV	μ/D	Transition nature	
DABNA-1	462.15	0.23	2.68	3.57	$S_1 \rightarrow S_0$	H→L（98.82%）
DABNA-P	556.66	0.11	2.23	2.04	$S_1 \rightarrow S_0$	H→L（99.44%）
DABNA-As	525.27	0.10	2.36	1.80	$S_1 \rightarrow S_0$	H→L（99.47%）
CzBN	490.85	0.46	2.53	7.50	$S_1 \rightarrow S_0$	H→L（99.33%）
CzBN-P	543.38	0.18	2.28	3.18	$S_1 \rightarrow S_0$	H→L（99.36%）
CzBN-As	554.54	0.10	2.24	1.85	$S_1 \rightarrow S_0$	H→L（99.49%）

Table S11 Cartesian coordinates of all studied compounds at optimized S_0 geometry.

DABNA-1			
C	1.221101	2.329798	-0.021669
C	0.000000	3.000496	-0.000001
C	-1.221101	2.329798	0.021668
C	-1.223957	0.922984	0.006767
C	0.000000	0.191587	0.000000
C	1.223957	0.922984	-0.006768
H	2.145892	2.892764	-0.034731
H	0.000000	4.087510	-0.000001
H	-2.145892	2.892764	0.034730
B	0.000000	-1.326211	0.000000
N	-2.439353	0.225201	0.008605
N	2.439353	0.225201	-0.008605
C	-2.545662	-1.165081	-0.163341
C	-3.833347	-1.739204	-0.288341
C	-1.381661	-1.989221	-0.224626
C	-3.976497	-3.097275	-0.536055
C	-1.588219	-3.358751	-0.521657
C	-2.848805	-3.918959	-0.680145
H	-4.975424	-3.513479	-0.637610
H	-0.719491	-3.994308	-0.656685
H	-2.960380	-4.974450	-0.911451
C	-3.655240	0.998206	0.115955
C	-4.280993	1.480119	-1.038898
C	-4.193660	1.262188	1.378948
C	-5.454970	2.229744	-0.925851
H	-3.847264	1.265686	-2.011050
C	-5.368252	2.012459	1.485610
C	-5.999008	2.496216	0.335017
H	-5.942696	2.604287	-1.821147

H	-5.788459	2.217823	2.465891
H	-6.911662	3.078964	0.420299
C	2.545662	-1.165081	0.163342
C	3.833347	-1.739204	0.288342
C	1.381662	-1.989221	0.224627
C	3.976497	-3.097275	0.536056
C	1.588219	-3.358751	0.521659
C	2.848805	-3.918958	0.680146
H	4.975425	-3.513479	0.637612
H	0.719491	-3.994308	0.656686
H	2.960380	-4.974450	0.911453
C	3.655240	0.998206	-0.115956
C	4.193660	1.262187	-1.378949
C	4.280993	1.480120	1.038897
C	5.368252	2.012458	-1.485611
C	5.454970	2.229745	0.925850
H	3.847264	1.265687	2.011050
C	5.999007	2.496216	-0.335018
H	5.788459	2.217822	-2.465892
H	5.942696	2.604287	1.821146
H	6.911662	3.078964	-0.420300
H	4.717521	-1.117929	0.209474
H	3.692811	0.880416	-2.263532
H	-4.717521	-1.117929	-0.209473
H	-3.692811	0.880417	2.263532

DABNA-P			
C	-1.119179	-2.448500	-0.462104
C	0.000130	-3.143482	-0.001289
C	1.119325	-2.448605	0.460019
C	1.137186	-1.046019	0.438633
C	-0.000089	-0.312239	-0.000360
C	-1.137236	-1.045906	-0.439782
H	-1.985485	-3.000221	-0.817989
H	0.000257	-4.230329	-0.001669
H	1.985694	-3.000446	0.815568
B	-0.000156	1.246022	-0.000109
C	2.586537	1.403944	0.277088
C	3.802261	2.088128	0.108025
C	1.361180	2.002198	-0.123362
C	3.830309	3.341092	-0.505030
C	1.429530	3.274593	-0.740092
C	2.639840	3.935205	-0.940899
H	4.780384	3.848445	-0.650685

H	0.509714	3.737869	-1.087453
H	2.659409	4.905558	-1.429332
C	4.016351	-1.088764	0.429511
C	4.152000	-1.277206	-0.958901
C	5.004949	-1.598361	1.286439
C	5.253849	-1.960977	-1.473848
H	3.393036	-0.887546	-1.631902
C	6.110382	-2.283621	0.768964
C	6.234782	-2.465020	-0.610080
H	5.349678	-2.101736	-2.547105
H	6.868881	-2.673202	1.442278
H	7.091801	-2.997073	-1.013844
C	-2.586786	1.403969	-0.277204
C	-3.802563	2.088061	-0.108012
C	-1.361459	2.002189	0.123337
C	-3.830636	3.340931	0.505209
C	-1.429842	3.274498	0.740263
C	-2.640170	3.935027	0.941142
H	-4.780708	3.848272	0.650947
H	-0.510050	3.737741	1.087727
H	-2.659789	4.905323	1.429689
C	-4.016306	-1.088884	-0.429188
C	-5.005374	-1.598376	-1.285631
C	-4.151087	-1.277616	0.959261
C	-6.110432	-2.283845	-0.767630
C	-5.252565	-1.961603	1.474730
H	-3.391765	-0.888018	1.631890
C	-6.233974	-2.465556	0.611453
H	-6.869307	-2.673340	-1.440570
H	-5.347729	-2.102598	2.548015
H	-7.090689	-2.997781	1.015632
H	-4.733190	1.631327	-0.435643
H	-4.909839	-1.458095	-2.359436
H	4.732911	1.631400	0.435606
H	4.908751	-1.458318	2.360217
P	-2.587693	-0.192556	-1.178643
P	2.587249	-0.192702	1.178286

DABNA-As			
C	1.088800	-2.482993	0.519879
C	0.000169	-3.184442	-0.001007
C	-1.088339	-2.482857	-0.521370
C	-1.109123	-1.083358	-0.485577
C	0.000002	-0.343715	0.000016

C	1.109450	-1.083637	0.484975
H	1.939510	-3.025025	0.926358
H	0.000316	-4.271266	-0.001315
H	-1.939163	-3.024443	-0.928356
B	-0.000218	1.220578	0.000176
C	-2.583560	1.464599	-0.359660
C	-3.776605	2.190889	-0.241902
C	-1.353940	2.002448	0.091134
C	-3.788156	3.431622	0.396362
C	-1.402799	3.264260	0.733913
C	-2.595839	3.965738	0.899131
H	-4.723077	3.974777	0.506825
H	-0.483444	3.690602	1.126674
H	-2.598848	4.925520	1.408648
C	-4.037576	-1.080489	-0.271695
C	-3.975049	-1.123131	1.130323
C	-5.127013	-1.667410	-0.927696
C	-4.987694	-1.743868	1.862543
H	-3.130946	-0.668622	1.641762
C	-6.144663	-2.290606	-0.194719
C	-6.074702	-2.328805	1.199717
H	-4.932186	-1.773077	2.947639
H	-6.986102	-2.743239	-0.712298
H	-6.862664	-2.811956	1.771023
C	2.583173	1.464697	0.359395
C	3.776199	2.190941	0.241214
C	1.353400	2.002729	-0.090605
C	3.787491	3.431887	-0.396695
C	1.401922	3.264767	-0.733117
C	2.594933	3.966299	-0.898671
H	4.722382	3.974961	-0.507530
H	0.482353	3.691235	-1.125301
H	2.597780	4.926166	-1.407735
C	4.038051	-1.080090	0.272097
C	5.127080	-1.667503	0.928291
C	3.976081	-1.122140	-1.129965
C	6.144867	-2.290575	0.195539
C	4.989005	-1.742782	-1.862027
H	3.132263	-0.667333	-1.641725
C	6.075532	-2.328138	-1.198956
H	6.986112	-2.743606	0.713284
H	4.934007	-1.771561	-2.947115
H	6.863766	-2.811192	-1.770087
H	4.703363	1.770365	0.624094

H	5.180500	-1.638420	2.013931
H	-4.703599	1.770624	-0.625421
H	-5.180955	-1.637904	-2.013354
As	2.635300	-0.216948	1.317739
As	-2.635508	-0.217159	-1.317923

CzBN			
C	-2.478149	0.851397	-0.207685
N	-2.433074	-0.525408	0.017887
C	-1.222691	-1.243143	-0.010960
C	0.000001	-0.497920	-0.000007
C	-1.366370	1.708834	-0.265829
C	1.222699	-1.243133	0.010934
N	2.433076	-0.525395	-0.017893
C	3.770986	-0.985285	-0.144279
C	4.290081	-2.226917	-0.532599
C	-1.214540	-2.643510	-0.076551
C	0.000017	-3.319594	-0.000049
C	1.214567	-2.643501	0.076478
C	-1.676934	3.060858	-0.542019
C	-2.992809	3.505654	-0.710170
H	3.662228	-3.055964	-0.828191
C	-4.076552	2.622942	-0.591863
H	-2.124965	-3.208078	-0.207989
C	-3.819954	1.276152	-0.330591
H	2.125003	-3.208063	0.207884
C	4.646167	0.108045	0.105987
H	-0.869539	3.780010	-0.641815
C	6.033383	-0.063617	0.045441
H	-5.094899	2.985065	-0.703942
C	6.547917	-1.315128	-0.289928
H	6.696621	0.773952	0.242587
C	5.679171	-2.374208	-0.592201
H	6.086983	-3.335047	-0.892582
C	-3.770987	-0.985292	0.144301
H	-3.662248	-3.055954	0.828273
C	2.478147	0.851408	0.207686
H	-6.086999	-3.335025	0.892668
C	-4.290092	-2.226911	0.532654
H	-6.696618	0.773950	-0.242590
C	-5.679182	-2.374195	0.592261
H	5.094895	2.985081	0.703930
C	-6.547924	-1.315120	0.289964
H	0.869532	3.780018	0.641805

C	-6.033384	-0.063619	-0.045431
C	-4.646167	0.108037	-0.105980
C	3.819953	1.276164	0.330588
C	4.076549	2.622956	0.591852
C	2.992803	3.505666	0.710156
C	1.676928	3.060867	0.542012
C	1.366366	1.708841	0.265829
B	-0.000003	1.044952	0.000007
H	0.000023	-4.405763	-0.000071
H	-7.622157	-1.465552	0.341139
H	7.622149	-1.465567	-0.341096
H	-3.180836	4.553713	-0.925204
H	3.180829	4.553727	0.925185

CzBN-P			
C	-2.534124	0.977127	0.167471
C	-1.145337	-1.415894	0.400542
C	0.000019	-0.654955	-0.000214
C	-1.362425	1.677966	-0.160587
C	1.145404	-1.415642	-0.401142
C	4.229914	-0.912607	-0.517938
C	5.025309	-2.037362	-0.758479
C	-1.128090	-2.816722	0.428514
C	0.000127	-3.515944	-0.000663
C	1.128265	-2.816521	-0.429586
C	-1.538187	2.885019	-0.873821
C	-2.815289	3.316180	-1.257663
H	4.609817	-2.914354	-1.247150
C	-3.949957	2.532680	-1.009069
H	-2.001382	-3.366270	0.769640
C	-3.813233	1.326782	-0.304321
H	2.001593	-3.365866	-0.770956
C	4.792810	0.249800	0.086979
H	-0.668014	3.465603	-1.170408
C	6.147983	0.248600	0.447327
H	-4.915976	2.846466	-1.396397
C	6.922493	-0.893321	0.235363
H	6.594728	1.130061	0.899673
C	6.364272	-2.034818	-0.355742
H	6.976089	-2.918628	-0.512404
C	-4.229777	-0.912741	0.518251
H	-4.609563	-2.914456	1.247653
C	2.534240	0.977248	-0.167825
H	-6.976020	-2.918667	0.513619

C	-5.025146	-2.037449	0.759087
H	-6.594933	1.129943	-0.898782
C	-6.364229	-2.034881	0.356721
H	4.915477	2.846603	1.396958
C	-6.922581	-0.893409	-0.234289
H	0.667544	3.465473	1.169757
C	-6.148089	0.248487	-0.446531
C	-4.792828	0.249638	-0.086560
C	3.813160	1.326947	0.304422
C	3.949593	2.532813	1.009295
C	2.814814	3.316225	1.257596
C	1.537843	2.884984	0.873360
C	1.362379	1.677971	0.159975
B	0.000002	0.940145	-0.000238
H	0.000130	-4.602417	-0.000842
H	-7.968877	-0.894282	-0.526563
H	7.968704	-0.894216	0.527939
H	-2.924421	4.247595	-1.806376
H	2.923711	4.247596	1.806429
P	-2.559836	-0.517002	1.160841
P	2.560195	-0.516873	-1.161070

CzBN-As			
C	-2.541718	1.071157	0.093348
C	-1.134106	-1.361385	0.420136
C	0.000000	-0.602226	0.000037
C	-1.353154	1.739176	-0.228389
C	1.134092	-1.361389	-0.420091
C	4.318115	-0.818421	-0.451452
C	5.162277	-1.904402	-0.687960
C	-1.117323	-2.759528	0.451609
C	-0.000015	-3.462732	0.000010
C	1.117298	-2.759531	-0.451583
C	-1.475767	2.882142	-1.049507
C	-2.725547	3.274772	-1.547968
H	4.814508	-2.755561	-1.267258
C	-3.870543	2.505118	-1.309377
H	-1.984651	-3.304076	0.815810
C	-3.781792	1.365764	-0.492239
H	1.984617	-3.304082	-0.815800
C	4.791753	0.314244	0.267777
H	-0.586064	3.436851	-1.338059
C	6.109165	0.316946	0.748582
H	-4.808089	2.776218	-1.788160

C	6.932835	-0.791025	0.539454
H	6.491357	1.176699	1.292785
C	6.461346	-1.903230	-0.168372
H	7.107136	-2.762826	-0.324210
C	-4.318128	-0.818404	0.451441
H	-4.814552	-2.755535	1.267252
C	2.541722	1.071151	-0.093332
H	-7.107163	-2.762787	0.324165
C	-5.162304	-1.904376	0.687942
H	-6.491320	1.176715	-1.292859
C	-6.461363	-1.903198	0.168330
H	4.808153	2.776226	1.788092
C	-6.932830	-0.790996	-0.539516
H	0.586118	3.436874	1.338093
C	-6.109146	0.316966	-0.748639
C	-4.791744	0.314257	-0.267808
C	3.781813	1.365760	0.492218
C	3.870592	2.505124	1.309338
C	2.725607	3.274789	1.547946
C	1.475812	2.882158	1.049524
C	1.353169	1.739178	0.228430
B	0.000002	1.000181	0.000054
H	-0.000021	-4.549415	-0.000001
H	-7.948454	-0.785509	-0.925256
H	7.948467	-0.785543	0.925175
H	-2.800365	4.156900	-2.177945
H	2.800445	4.156926	2.177907
As	-2.609428	-0.410845	1.277214
As	2.609403	-0.410856	-1.277194

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