

Aromatic Pathways in Mono- and Bisphosphorous Singly Möbius Twisted [28] and [30]Hexaphyrins[†]

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Received Xth XXXXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXXX 20XX

First published on the web Xth XXXXXXXXXXXX 200X

DOI: 10.1039/b000000x

1 Molecular structures

The Cartesian coordinates (in Å) of the hexaphyrins optimized at the B3LYP/def2-TZVP level.

Monophosphorous [28]hexaphyrin

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C	-1.1319621	5.4064313	0.6784493
C	-0.6724893	4.4795644	-0.2574599
C	0.0979920	4.9785827	-1.3091593
C	0.3838984	6.3298518	-1.4413180
C	-0.0995596	7.2262425	-0.4967401
C	-0.8580138	6.7640983	0.5694974
C	-0.9900470	3.0178396	-0.1550556
C	0.0924737	2.1923030	0.2549408
C	0.3651717	0.8204882	0.1062521
C	1.6931434	0.5952532	0.4926765
C	2.2211536	1.8324610	0.9587718
N	1.2359145	2.7557243	0.7986964
P	2.7245977	-0.8353596	0.6792456
O	2.4704115	-1.6923463	1.8393184
C	3.5108615	2.1054614	1.4813754
C	3.8072382	3.4110638	2.1205994
C	4.6780209	4.3440348	1.5530137
C	4.9709791	5.5533396	2.1684159
C	4.3775863	5.8656571	3.3837467
C	3.4973523	4.9679310	3.9731285
C	3.2258294	3.7625448	3.3419332
F	5.2551097	4.0909702	0.3741812
F	5.8078881	6.4180922	1.5965077
F	4.6495927	7.0215735	3.9805336
F	2.9321366	5.2625266	5.1423804
F	2.3919801	2.9136727	3.9472334

F	0.5679741	4.1453351	-2.2408617
F	1.1095511	6.7733868	-2.4669525
F	0.1679126	8.5238572	-0.6120823
F	-1.3144212	7.6223133	1.4810713
F	-1.8540828	4.9998960	1.7252064
N	2.9815265	-1.7424524	-0.7704689
C	4.2668250	-2.1232428	-1.1904717
C	4.1248978	-2.8067514	-2.4018517
C	2.7780046	-2.8107731	-2.7410615
C	2.0592203	-2.2100069	-1.7081625
C	5.4588227	-1.7364309	-0.5193203
C	5.4366350	-0.7047466	0.3864382
N	4.2300480	-0.0460665	0.6594905
C	4.4974020	1.1521228	1.3172324
C	5.9053122	1.1703508	1.5724188
C	6.4668548	0.0549530	1.0196787
C	0.6302439	-2.1695732	-1.5470115
C	0.0079588	-2.6193514	-0.3880827
N	-1.3096222	-2.3896066	-0.1069705
C	-1.6208526	-3.2027706	0.9123699
C	-0.4554351	-3.9740836	1.3421516
C	0.5690649	-3.5778430	0.5639628
C	-2.9277224	-3.3071710	1.4536714
C	-3.2330412	-4.4334700	2.3774450
C	-3.2408461	-5.7588747	1.9395341
C	-3.5070634	-6.8191912	2.7938179
C	-3.7775639	-6.5689717	4.1320506
C	-3.7798407	-5.2636663	4.6028478
C	-3.5104377	-4.2200415	3.7284901
F	-3.0068938	-6.0392463	0.6543172
F	-3.5160902	-8.0727173	2.3379444
F	-4.0358102	-7.5778876	4.9608412
F	-4.0310183	-5.0225907	5.8904373
F	-3.5014629	-2.9796748	4.2265702
C	6.7389055	-2.3860633	-0.8980286
C	7.0018431	-3.7097534	-0.5428851
C	8.1887306	-4.3427334	-0.8817265
C	9.1543152	-3.6484563	-1.5981265
C	8.9247336	-2.3312791	-1.9697843

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				Bisphosphorous [30]hexaphyrin			
C	7.7285972	-1.7199193	-1.6205954				
F	6.1027986	-4.4017206	0.1604123				
F	8.4118342	-5.6050322	-0.5176864				
F	10.2970773	-4.2439310	-1.9265194	118			
F	9.8479463	-1.6658050	-2.6639631	N	1.6551827	1.8070171	0.1974730
F	7.5368514	-0.4562875	-2.0137867	C	1.9782891	2.8266767	1.1730318
C	-0.1702686	-1.7684041	-2.7212600	C	0.8191253	3.6475928	1.3462581
C	-1.2280276	-2.5506004	-3.2049259	C	-0.1236978	3.2706592	0.4647985
C	-1.9864531	-2.1673016	-4.3000394	C	0.3713514	2.1699857	-0.3296686
C	-1.7007101	-0.9790573	-4.9578920	C	3.2230294	3.0079338	1.7062256
C	-0.6474446	-0.1882429	-4.5220917	C	3.5093899	4.1162360	2.6488086
C	0.1021499	-0.5916217	-3.4296251	C	3.4587521	5.4571414	2.2671001
F	-1.5032913	-3.7340565	-2.6589618	C	3.7474263	6.4877214	3.1505542
F	-2.9761058	-2.9447377	-4.7413140	C	4.1094997	6.1894590	4.4563399
F	-2.4243546	-0.6066416	-6.0098472	C	4.1793684	4.8654048	4.8678874
F	-0.3704763	0.9562709	-5.1491259	C	3.8829787	3.8522677	3.9680992
F	1.0908394	0.2180236	-3.0335291	C	-0.2413862	1.7122000	-1.4652146
C	-3.9513188	-2.4228100	1.1335609	C	0.4779104	0.9549819	-2.5117028
C	-5.3615054	-2.5703655	1.3767632	C	1.6796241	1.4240901	-3.0595229
C	-5.9993763	-1.5082932	0.8189627	C	2.3330501	0.7659582	-4.0896556
C	-5.0026489	-0.6290272	0.2628743	C	1.7993463	-0.4066235	-4.6049623
N	-3.7958574	-1.2346932	0.4716038	C	0.6030726	-0.8963794	-4.1007144
C	-5.1988245	0.6197781	-0.3123167	C	-0.0412660	-0.2143103	-3.0819123
C	-6.6119217	1.0122155	-0.6004395	F	3.1389850	5.7875844	1.0111061
C	-7.2760288	0.5452571	-1.7336744	F	3.6911679	7.7587598	2.7497669
C	-8.5873003	0.8982793	-2.0219962	F	4.3904193	7.1694612	5.3112411
C	-9.2724083	1.7430521	-1.1603536	F	4.5216566	4.5783559	6.1238405
C	-8.6428600	2.2256971	-0.0213738	F	3.9471791	2.5926396	4.4012561
C	-7.3311446	1.8573270	0.2432965	F	2.2132521	2.5703880	-2.6296100
F	-6.6451294	-0.2620526	-2.5924826	F	3.4567703	1.2630446	-4.6035259
F	-9.1894607	0.4366953	-3.1188461	F	2.4258653	-1.0527071	-5.5856170
F	-10.5304970	2.0886552	-1.4243642	F	0.0854307	-2.0218151	-4.5948792
F	-9.3031080	3.0322174	0.8109546	F	-1.1957779	-0.7199002	-2.6375306
F	-6.7625349	2.3316297	1.3559325	P	2.4345714	0.3175249	0.7596363
C	-4.1750578	1.5694182	-0.5693520	O	1.9538816	-0.0514640	2.0879825
N	-2.8776055	1.4251017	-0.2382623	C	4.2949301	2.1765825	1.2689095
C	-2.2936775	2.6413859	-0.4718420	C	5.6581564	2.3889013	1.1158546
C	-3.2693242	3.5687805	-1.0397633	C	6.1634362	1.3659776	0.3001256
C	-4.4354975	2.8989610	-1.1129966	C	5.1146176	0.5121079	-0.0219385
H	2.3295865	-3.2681956	-3.6079931	N	3.9807848	0.9876194	0.6210636
H	4.9372469	-3.2289211	-2.9702424	C	5.0105477	-0.6245309	-0.8543248
H	7.5163915	-0.1870620	0.9867860	C	6.2316935	-1.0873258	-1.5694845
H	6.4278195	1.9752171	2.0625575	C	6.6519746	-0.4760801	-2.7492665
H	-0.3417484	0.1005477	-0.2640226	C	7.8036002	-0.8701703	-3.4162172
H	-3.0820563	4.5837213	-1.3504522	C	8.5728034	-1.9031182	-2.8986131
H	-5.3786931	3.2649224	-1.4850380	C	8.1863687	-2.5303354	-1.7221772
H	-7.0596552	-1.3186220	0.8121537	C	7.0312229	-2.1160982	-1.0734645
H	-5.8126439	-3.4048953	1.8870300	F	5.9323973	0.5179337	-3.2741406
H	-0.4284003	-4.7026801	2.1366706	F	8.1729733	-0.2683954	-4.5466479
H	1.5852194	-3.9312536	0.5857090	F	9.6780539	-2.2914421	-3.5288146
H	1.3322093	3.7305723	1.0264659	F	8.9267850	-3.5204173	-1.2229295
H	-2.9049877	-0.8662252	0.1599378	F	6.6958895	-2.7350723	0.0623861
				C	3.8461082	-1.3352617	-0.9476551

C	3.7304982	-2.6443556	-1.4994689	C	-3.9196729	2.1817265	-1.5912996
C	2.6399047	-3.2394584	-0.9805371	C	-3.5380181	2.7868376	-2.7804896
C	1.9033688	-2.3316869	-0.1478557	C	-2.1419711	2.6851375	-2.8890209
N	2.6190549	-1.0592582	-0.2336651	C	-1.6480960	2.0542893	-1.7623118
C	0.7568118	-2.7519282	0.5015868	N	-2.7480518	1.7225225	-0.9648293
C	0.5673000	-4.2281756	0.6331375	H	-1.5345813	3.0434373	-3.7044908
C	-0.4140786	-4.9152193	-0.0858467	H	-4.2095501	3.2198527	-3.5032861
C	-0.6213999	-6.2794280	0.0580675	H	-7.6102218	0.6468997	0.2728808
C	0.1682356	-7.0012577	0.9436552	H	-6.8203598	-1.2698481	1.9018470
C	1.1535592	-6.3531833	1.6752843	H	0.0395040	-0.1242305	-0.1669418
C	1.3410516	-4.9863621	1.5155312	H	2.3154105	-4.2461901	-1.1791604
F	-1.1722377	-4.2590726	-0.9699461	H	4.4610779	-3.0890047	-2.1542946
F	-1.5589981	-6.9027160	-0.6552720	H	7.1774186	1.2636643	-0.0494228
F	-0.0199429	-8.3093991	1.0896552	H	6.2024121	3.2358013	1.4995300
F	1.9061017	-7.0436944	2.5305213	H	0.7703392	4.4866361	2.0200284
F	2.2901001	-4.4027846	2.2476379	H	-1.0699198	3.7512938	0.2925291
C	-0.3497408	-1.9475677	0.9104147	H	-1.6070060	-3.2883637	1.9879974
C	-0.6046189	-0.6733551	0.4757544				
C	-1.8959498	-0.3165343	0.8473299				
C	-2.4640526	-1.4122825	1.5225746				
N	-1.4840436	-2.3746526	1.5852962				
C	-3.8419359	-1.5509878	1.8927787				
C	-4.2896391	-2.6976012	2.7168832				
C	-5.1500474	-3.6844324	2.2284052				
C	-5.5718901	-4.7527413	3.0075208				
C	-5.1219146	-4.8684854	4.3151621				
C	-4.2557185	-3.9147214	4.8323786				
C	-3.8544886	-2.8511598	4.0368309				
P	-2.8167681	1.1494322	0.6493472				
O	-2.6618686	2.2285088	1.6305442				
F	-5.5873385	-3.6294040	0.9659224				
F	-6.3937130	-5.6736153	2.5041212				
F	-5.5173418	-5.8900944	5.0690225				
F	-3.8279769	-4.0190961	6.0899367				
F	-3.0380381	-1.9422625	4.5758323				
C	-4.7413929	-0.6432752	1.3684584				
C	-6.1827579	-0.5850373	1.3673861				
C	-6.5915719	0.4058037	0.5292342				
C	-5.4310538	1.0307852	-0.0486050				
N	-4.3275628	0.4116254	0.5503375				
C	-5.2372969	1.9188966	-1.0710513				
C	-6.3955864	2.5695393	-1.7347742				
C	-6.6404379	3.9343888	-1.5801864				
C	-7.7098308	4.5667049	-2.1973267				
C	-8.5728534	3.8294239	-2.9967810				
C	-8.3590374	2.4698739	-3.1723858				
C	-7.2804201	1.8601396	-2.5464500				
F	-5.8416792	4.6705048	-0.8046516				
F	-7.9206470	5.8711670	-2.0202575				
F	-9.6037370	4.4246449	-3.5911899				
F	-9.1836968	1.7609806	-3.9443624				
F	-7.0981868	0.5516457	-2.7547556				

2 Calculated NMR shieldings

Calculated B3LYP/def2-TZVP nuclear magnetic resonance shieldings in ppm. Tetramethylsilane (TMS) reference shieldings obtained at the same level of theory are 183.746 ppm (^{31}C) and 31.913 ppm (^1H).

Monophosphorous [28]hexaphyrin

NO.	TYPE	ISOTROPIC
1	c	24.95507295
2	c	57.54371399
3	c	26.50171487
4	c	36.22460504
5	c	31.40447721
6	c	35.89907962
7	c	66.05791079
8	c	46.11719600
9	c	47.59987998
10	c	66.18819240
11	c	38.51286004
12	n	94.74169677
13	p	300.80822858
14	o	98.15715723
15	c	89.93509480
16	c	65.02526356
17	c	26.88132075
18	c	35.39642267
19	c	31.16345736
20	c	34.93814961
21	c	25.42429705
22	f	311.48747087
23	f	337.52048152
24	f	325.16860223

25	f	339.87841725	77	c	28.68155546
26	f	311.01246229	78	f	304.85941464
27	f	309.18509441	79	f	342.65050585
28	f	340.20212725	80	f	328.04135543
29	f	327.11608563	81	f	346.21471849
30	f	339.38849663	82	f	313.71483189
31	f	311.06861526	83	c	33.36270074
32	n	49.87614019	84	c	50.30230139
33	c	38.66741333	85	c	49.01653795
34	c	52.56503220	86	c	32.51129693
35	c	57.08297285	87	n	90.65746370
36	c	48.94280178	88	c	76.80505933
37	c	80.47222501	89	c	58.39113975
38	c	42.09075641	90	c	25.30389987
39	n	101.78692286	91	c	36.61039927
40	c	40.03977885	92	c	31.65017281
41	c	54.86265505	93	c	36.51519564
42	c	55.00968311	94	c	24.47810685
43	c	61.47759841	95	f	311.34444044
44	c	13.48179707	96	f	343.57524898
45	n	-72.32710180	97	f	328.41453098
46	c	3.30305070	98	f	343.36813782
47	c	49.65398346	99	f	310.15575167
48	c	42.98608049	100	c	14.03391767
49	c	77.20246392	101	n	-23.71959220
50	c	59.70898733	102	c	22.44530282
51	c	25.24399118	103	c	44.42367250
52	c	36.01387828	104	c	47.40665698
53	c	31.67912930	105	h	24.80979685
54	c	36.31666308	106	h	23.58954899
55	c	26.37113896	107	h	23.36747885
56	f	310.12866231	108	h	23.43175105
57	f	343.64751850	109	h	32.88487225
58	f	328.47640445	110	h	24.21106090
59	f	344.02008511	111	h	24.19933395
60	f	314.88650906	112	h	23.88541538
61	c	63.73275037	113	h	23.97628391
62	c	24.29871109	114	h	25.20241056
63	c	35.17247190	115	h	24.87165676
64	c	30.96205396	116	h	22.44338995
65	c	35.87197596	117	h	28.99676062
66	c	26.34372253			
67	f	309.86420216			
68	f	341.03118306			
69	f	326.00760654			
70	f	341.25218411			
71	f	315.41937761			
72	c	61.15318638			
73	c	33.47271872			
74	c	37.76710602			
75	c	32.18478855			
76	c	38.18435247			

Bisphosphorous [30]hexaphyrin

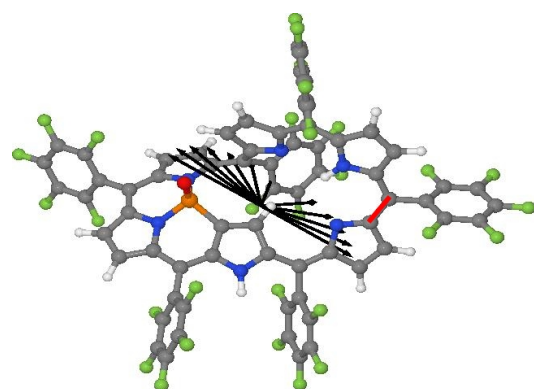
NO.	TYPE	ISOTROPIC
1	n	90.51700758
2	c	16.52994483
3	c	56.92333573
4	c	38.06333686
5	c	19.79571898
6	c	66.88260707
7	c	65.57276982

8	c	26.87835188	60	c	26.81772908
9	c	35.91220727	61	f	311.10833629
10	c	31.67296005	62	f	340.62482101
11	c	35.29828975	63	f	327.21582012
12	c	25.59198666	64	f	338.03004660
13	c	75.92165826	65	f	310.68093822
14	c	58.69368279	66	c	37.36624187
15	c	20.87324196	67	c	51.29907206
16	c	34.26192809	68	c	69.36192493
17	c	30.13661706	69	c	36.86455362
18	c	33.06085334	70	n	101.34834592
19	c	26.30809348	71	c	82.74450322
20	f	315.92261583	72	c	67.78065138
21	f	342.57666574	73	c	28.43274914
22	f	328.14270023	74	c	35.96419832
23	f	339.93879986	75	c	32.38433357
24	f	306.12945050	76	c	35.36039721
25	f	307.64257054	77	c	26.64666809
26	f	335.08298839	78	p	290.80572339
27	f	329.26594845	79	o	58.27132439
28	f	340.57192123	80	f	312.03898415
29	f	308.94670906	81	f	338.85021760
30	p	287.26645697	82	f	327.64229019
31	o	96.14006888	83	f	340.64470289
32	c	32.31249420	84	f	308.97761740
33	c	66.73624865	85	c	29.10139325
34	c	68.01341966	86	c	54.14013310
35	c	42.56446922	87	c	52.05433755
36	n	67.27060884	88	c	35.00697495
37	c	76.14750940	89	n	88.46546039
38	c	65.35190425	90	c	70.54557030
39	c	26.46729422	91	c	64.51281336
40	c	35.53476440	92	c	26.23976382
41	c	31.44839828	93	c	35.77056842
42	c	36.29250226	94	c	32.07630047
43	c	26.89090105	95	c	36.05179078
44	f	311.38223201	96	c	27.74814128
45	f	341.15444689	97	f	309.75243356
46	f	326.69611765	98	f	341.83070397
47	f	340.47596937	99	f	327.50119309
48	f	314.26492209	100	f	342.61756260
49	c	24.31927410	101	f	315.77802934
50	c	50.98443750	102	c	38.38449139
51	c	47.06127010	103	c	76.61454091
52	c	24.04039083	104	c	62.53275992
53	n	76.99139588	105	c	36.51943452
54	c	73.30115275	106	n	60.17518619
55	c	62.27113995	107	h	25.68348276
56	c	28.32374758	108	h	26.72053476
57	c	36.20537841	109	h	26.03310570
58	c	32.05106861	110	h	26.29713672
59	c	35.86984520	111	h	17.15350650

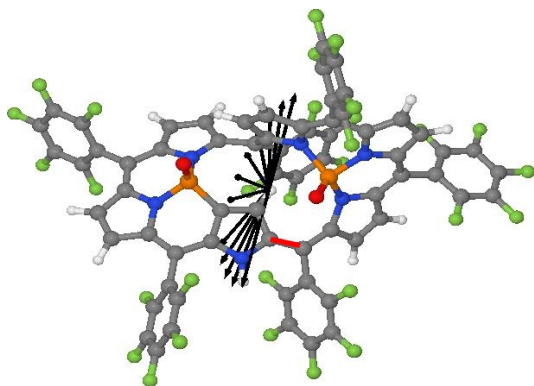
112	h	27.13625910
113	h	26.64711728
114	h	26.78945979
115	h	26.79500074
116	h	25.99992850
117	h	24.84491639
118	h	26.90519271

3 Details for Figure 3 of main manuscript

Figure 1 illustrates at which bond (red) the integration plane for obtaining the current strength function with respect to the applied magnetic field (black arrows) was placed. The integration planes were placed perpendicular to bond C₈₀–C₁₀₀ for (PO)[28]hp and bond C₅₄–C₆₆ for (PO)₂[30]hp. The x, y, z components of the applied magnetic field are given below.



(a) Monophosphorous [28]hexaphyrin, (PO)[28]hp



(b) Bisphosphorous [30]hexaphyrin, (PO)₂[30]hp

Fig. 1 Illustration of the relative orientation and placement of the external magnetic field (black arrows) for obtaining the current strength function. The integration planes were placed perpendicular to bond C₈₀–C₁₀₀ for (PO)[28]hp and bond C₅₄–C₆₆ for (PO)₂[30]hp. The respective bonds are marked red.

B field components used for (PO)[28]hp

B_x	B_y	B_z
0.69249	-0.68669	0.22117
0.67501	-0.73701	-0.03439
0.61152	-0.73710	-0.28761
0.50636	-0.68697	-0.52122
0.36670	-0.59001	-0.71932
0.20204	-0.45285	-0.86839
0.02361	-0.28483	-0.95829
-0.15642	-0.09740	-0.98288
-0.32580	0.09667	-0.94048
-0.47297	0.28415	-0.83400
-0.58791	0.45227	-0.67068
-0.66279	0.58957	-0.46165
-0.69249	0.68669	-0.22117

B field components used for (PO)₂[30]hp

B_x	B_y	B_z
0.37461	0.77445	-0.50979
0.23012	0.67357	-0.70239
0.06994	0.52678	-0.84712
-0.09500	0.34409	-0.93412
-0.25346	0.13796	-0.95746
-0.39465	-0.07758	-0.91555
-0.50895	-0.28783	-0.81125
-0.58856	-0.47847	-0.65166
-0.62807	-0.63650	-0.44766
-0.62477	-0.75115	-0.21316
-0.57889	-0.81461	0.03587
-0.49357	-0.82256	0.28246
-0.37461	-0.77445	0.50979