SUPPORTING INFORMATION

The Molecular Structure of the *trans* and *cis* Isomers of Metal-Free Phthalocyanine Studied by Gas-Phase Electron Diffraction and High-Level Quantum Chemical Calculations. NH Tautomerization and Calculated Vibrational Frequencies.

Tatyana Strenalyuk, Svein Samdal* and Hans Vidar Volden

TABLE S1: Selected Interatomic Distanses (pm) for H_2Pc

	B3LYP/6-311++G**[a]				B3LYP/cc-pVTZ[b]	
	trans(D_{2h})	TS(C_s)	TS(D_{2h})	*cis*(C_{2v})	*trans*(D_{2h})	*cis*(C_{2v})
N1··N2	281.23	305.88	244.65	303.45	281.00	303.44
N1··N3	404.78	398.75	395.21	399.02	404.74	398.70
N2··N4	390.52	393.44	395.21	399.02	389.92	398.70
N3··N4	281.23	301.64	244.65	294.65	281.00	294.27
H57··H58	202.29	210.92	278.56	189.00	202.88	189.57
N1-H57	101.24	102.42	128.98	102.76	100.93	102.43
N2-H58		127.97	128.98	102.76		102.43
N3-H58	101.24	133.37	128.98		100.93	
C21-H37	108.30	108.30	108.29	108.30	108.06	108.06
C23-H39	108.41	108.34	108.31	108.40	108.07	108.06
C29-H45	108.33	108.45	108.45	108.30	108.17	108.16
C31-H47	108.43	108.43	108.41	108.41	108.19	108.17
N1-C5	137.66	137.31	137.16	137.72	137.32	137.35
N1-C6	137.66	137.63	137.43	138.37	137.32	137.99
N2-C7	136.27	136.41	137.43	138.37	135.98	137.99
N2-C8	136.29	135.08	137.16	137.72	135.98	137.35
N3-C9	137.66	137.77	137.16	136.20	137.32	135.90
N3-C10	137.66	137.34	137.43	135.78	137.32	135.47
N4-C11	136.29	137.62	137.43	135.78	135.98	135.47
N4-C12	136.29	138.56	137.16	136.20	135.98	135.90
C5-C13	145.20	145.12	146.38	144.53	144.92	144.24
C6-C14	145.20	144.69	145.09	144.98	144.92	144.70
C7-C15	146.63	146.65	145.09	144.98	146.37	144.70
C8-C16	146.63	147.28	146.38	144.53	146.37	144.24
C9-C17	145.20	146.89	146.38	146.81	144.92	146.55
C10-C18	145.20	145.36	145.09	147.68	144.92	147.39
C11-C19	146.63	144.75	145.09	147.68	146.37	147.39
C12-C20	146.63	145.90	146.38	146.81	146.37	146.55
C13-C14	141.17	141.35	140.48	141.31	140.85	140.99
C15-C16	140.27	140.38	140.48	141.31	139.92	140.99
C17-C18	141.17	140.18	140.48	140.23	140.85	139.88
C19-C20	140.27	140.40	140.48	140.23	139.92	139.88
C13-C21	139.61	139.71	139.39	139.76	139.24	139.40
C14-C22	139.61	139.72	139.43	139.81	139.24	139.43
C15-C23	139.14	139.06	139.43	139.81	138.75	139.43
C16-C24	139.14	139.01	139.39	139.76	138.75	139.40

C17-C25	139.61	139.26	139.39	138.98	139.24	138.59
C18-C26	139.61	139.32	139.43	138.95	139.24	138.54
C19-C27	139.14	139.56	139.43	138.95	138.75	138.54
C20-C28	139.14	139.56	139.39	138.98	138.75	138.59
C21-C29	138.91	138.83	139.18	138.77	138.53	138.37
C22-C30	138.91	138.82	139.15	138.78	138.53	138.39
C23-C31	139.49	139.59	139.15	138.78	139.13	138.39
C24-C32	139.49	139.61	139.18	138.77	139.13	138.37
C25-C33	138.90	139.30	139.18	139.66	138.53	139.29
C26-C34	138.90	139.27	139.15	139.68	138.53	139.31
C27-C35	139.49	139.02	139.15	139.68	139.13	139.31
C28-C36	139.49	139.05	139.18	139.66	139.13	139.29
C29-C30	140.84	140.95	140.64	141.00	141.00	140.62
C31-C32	140.35	140.25	140.64	141.00	139.95	140.62
C33-C34	140.84	140.54	140.64	140.18	140.47	139.78
C35-C35	140.35	140.79	140.64	140.18	139.95	139.78
C6-N53	131.50	132.17	132.71	131.73	131.20	131.44
C7-N53	133.37	133.16	132.71	131.73	133.09	131.44
C8-N54	133.37	132.76	131.89	132.29	133.09	132.03
C9-N54	131.50	131.89	131.89	133.20	131.20	132.93
C10-N55	131.50	132.45	132.71	132.74	131.20	132.46
C11-N55	133.37	132.85	132.71	132.74	133.09	132.46
C12-N56	133.37	132.10	131.89	133.20	133.09	132.93
C5-N56	131.50	131.43	131.89	132.29	131.20	132.03

[a] Energies (hartree). *trans* (D_{2h}): Electronic (E_{el}) = -1668.730803, zero-point correction (E_o) = 0.433825, termal correction to Gibbs free energy (E_G) = 0.377977; *cis*(C_{2v}): E_{el} = -1668.716240, E_o = 0.433045, E_G = 0.376696; TS(C_s): E_{el} = -1668.706365; TS(D_{2h}): E_{el} = -1668.694321. [b] *trans*(D_{2h}): E_{el} = -1668.877707, *cis*(C_{2v}): E_{el} = -1668.863517

TABLE S2: Selected Bond Angles (degree) for H_2Pc

	B3LYP/6-311++G**				B3LYP/cc-pVTZ	
	trans(D_{2h})	TS(C_s)	TS(D_{2h})	*cis*(C_{2v})	*trans*(D_{2h})	*cis*(C_{2v})
C5-N1-C6	112.53	112.25	108.78	112.06	112.61	112.15
C7-N2-C8	107.21	107.82	108.78	112.06	107.31	112.15
C9-N3-C10	112.53	108.37	108.78	107.84	112.61	107.94
C11-N4-C12	107.21	108.39	108.78	107.84	107.31	107.94
C6-N53-C7	124.10	120.78	118.35	128.27	124.25	128.52
C8-N54-C9	124.10	127.27	128.96	121.40	124.25	121.52
C10-N55-C11	124.10	118.82	118.35	126.13	124.25	126.28
C12-N56-C5	124.10	128.48	128.96	121.40	124.25	121.52
N1-C5-C13	106.14	106.20	108.39	106.77	106.09	106.74
N1-C5-C14	106.14	106.65	109.85	105.92	106.09	105.87
N2-C7-C15	110.74	110.60	109.86	105.92	110.66	105.87
N2-C8-C16	110.74	110.40	108.39	106.77	110.66	106.74
N3-C9-C17	106.14	108.33	108.39	110.80	106.09	110.71
N3-C10-C18	106.14	110.34	109.85	110.00	106.09	109.94
N4-C11-C19	110.74	109.98	109.85	110.00	110.66	109.94
N4-C12-C20	110.74	108.20	108.39	110.80	110.66	110.71
C5-C13-C14	107.60	107.72	107.21	107.25	107.60	107.24
C6-C14-C13	107.60	107.19	105.78	108.00	107.60	108.01
C7-C15-C16	105.66	105.36	105.78	108.00	105.68	108.01
C8-C16-C15	105.66	105.82	107.21	107.25	105.68	107.24
C9-C17-C18	107.60	107.37	107.21	105.29	107.60	105.33
C10-C18-C17	107.60	105.59	105.78	106.07	107.60	106.09
C11-C19-C20	105.66	105.97	105.78	106.07	105.68	106.09
C12-C20-C19	105.66	107.45	107.21	105.25	105.68	105.33
C13-C14-C22	120.97	121.00	121.32	120.75	120.94	120.73
C14-C13-C21	120.97	120.83	120.98	121.06	120.94	121.03
C15-C16-C24	121.23	121.16	120.98	121.06	121.21	121.03
C16-C15-C23	121.23	121.28	121.32	120.75	121.21	120.73
C17-C18-C26	120.97	121.45	121.32	121.15	120.94	121.14
C18-C17-C25	120.97	121.04	120.98	121.38	120.94	121.34
C19-C20-C28	121.23	120.92	120.98	121.38	121.21	121.34
C20-C19-C27	121.23	121.37	121.32	121.15	121.21	121.14
C13-C21-C29	117.81	117.88	117.75	117.83	117.85	117.87
C14-C22-C30	117.81	117.82	117.60	117.90	117.85	117.93
C15-C23-C31	117.65	117.64	117.60	117.90	117.69	117.93
C16-C24-C32	117.65	117.71	117.75	117.83	117.69	117.87

C17-C25-C33	117.81	117.69	117.75	117.59	117.85	117.63
C18-C26-C34	117.81	117.51	117.60	117.69	117.85	117.72
C20-C28-C36	117.65	117.74	117.75	117.59	117.69	117.63
C21-C29-C30	121.22	121.26	121.20	121.16	121.21	121.15
C22-C30-C29	121.22	121.21	121.15	121.30	121.21	121.29
C23-C31-C32	121.12	121.11	121.15	121.30	121.11	121.29
C24-C32-C31	121.12	121.11	121.20	121.16	121.11	121.15
C25-C33-C34	121.22	121.19	121.20	121.08	121.21	121.07
C26-C34-C33	121.22	121.12	121.15	121.11	121.21	121.10
C27-C35-C36	121.12	121.11	121.15	121.11	121.11	121.10
C28-C36-C35	121.12	121.25	121.20	121.08	121.11	121.08
C5-N1-N57	123.74	129.98	146.22	115.66	123.69	115.60

TABLE S3: Calculated Vibrational Frequencies (cm^{-1}), IR Intensities (km/mol) and Raman Intensities ($Å^4$/amu) for *trans* and *cis* Isomers of H_2Pc

	trans				*cis*				*trans*					*cis*			
No	sym	freq	IR	Raman	sym	freq	IR	Raman	No	sym	freq	IR	Raman	sym	freq	IR	Raman
1	A_g	3602	0	12	A_1	3323	187	39	85	B_{3u}	978	2	0	B_1	977	2	0
2	B_{1u}	3544	131	0	B_2	3274	24	11	86	B_{2g}	978	0	0	A_2	976	0	0
3	A_g	3203	0	784	A_1	3202	19	745	87	B_{3u}	971	2	0	B_1	972	2	0
4	B_{1u}	3203	40	0	B_2	3201	22	38	88	B_{1g}	971	0	0	A_2	971	0	0
5	B_{2u}	3200	9	0	A_1	3199	6	171	89	B_{3g}	905	0	2	A_1	939	6	38
6	B_{3g}	3200	0	173	B_2	3198	3	1	90	A_u	892	0	0	B_1	894	0	0
7	A_g	3198	0	713	A_1	3198	31	594	91	B_{2g}	892	0	0	A_2	894	0	0
8	B_{2u}	3198	49	0	B_2	3198	14	29	92	B_{1u}	891	59	0	B_1	888	1	0
9	B_{1u}	3195	13	0	A_1	3194	0	211	93	B_{1g}	890	0	0	A_2	887	0	0
10	B_{3g}	3195	0	168	B_2	3194	15	12	94	A_u	890	0	0	B_2	883	18	0
11	A_g	3184	0	701	A_1	3183	14	353	95	B_{2u}	855	0	0	A_1	872	4	44
12	B_{1u}	3184	31	0	B_2	3183	15	343	96	B_{3g}	841	0	1	B_2	854	1	5
13	A_g	3181	0	661	A_1	3180	23	326	97	A_g	810	0	172	B_1	851	78	1
14	B_{2u}	3181	37	0	B_2	3180	16	337	98	B_{3u}	809	44	0	A_1	808	4	101
15	B_{3g}	3171	0	229	A_1	3169	5	218	99	B_{2u}	804	2	0	A_2	805	0	7
16	B_{2u}	3171	7	0	B_2	3169	2	1	100	B_{1u}	799	8	0	B_2	803	8	1
17	B_{1u}	3167	6	0	A_1	3166	3	196	101	B_{1g}	788	0	19	A_1	794	5	15
18	B_{3g}	3167	0	197	B_2	3166	3	3	102	A_u	788	0	0	B_1	793	14	6
19	B_{3g}	1650	0	78	A_1	1652	13	140	103	B_{2g}	787	0	5	A_2	787	0	0
20	B_{2u}	1650	15	0	B_2	1648	11	11	104	B_{3u}	782	183	0	B_1	786	71	2
21	B_{1u}	1642	11	0	A_1	1642	4	10	105	B_{2g}	780	0	7	A_2	783	0	2
22	B_{3g}	1642	0	0	B_2	1641	2	13	106	A_u	780	0	0	B_1	780	42	4
23	A_g	1629	0	35	A_1	1632	6	32	107	B_{3u}	779	0	0	A_2	778	0	4

24	B_{2u}	1629	13	0	B_2	1631	6	103	108	A_g	779	0	12	B_2	777	0	41
25	A_g	1614	0	146	B_2	1611	15	1301	109	B_{1g}	778	0	0	A_2	765	0	0
26	B_{1u}	1613	4	0	A_1	1611	1	89	110	B_{2u}	750	65	0	B_1	776	2	3
27	A_g	1592	0	19278	B_2	1603	68	7240	111	B_{1u}	745	69	0	B_2	755	27	281
28	B_{2u}	1575	5	0	B_2	1584	110	6808	112	A_g	742	0	1156	A_1	744	38	71
29	B_{3g}	1574	0	4	A_1	1582	13	346	113	B_{2g}	738	0	1	B_1	741	141	1
30	A_g	1545	0	1731	A_1	1547	2	817	114	B_{3u}	737	145	0	A_2	724	0	3
31	B_{1u}	1539	116	0	B_2	1543	88	550	115	B_{1g}	733	0	3	B_2	722	48	599
32	B_{2u}	1536	32	0	A_1	1532	31	832	116	B_{2g}	716	0	3	B_1	717	26	2
33	B_{3g}	1511	0	158	B_2	1511	10	39	117	B_{3g}	697	0	4	A_1	698	1	7
34	B_{2u}	1510	8	0	A_1	1510	8	255	118	A_g	691	0	385	A_2	689	0	1
35	B_{1u}	1501	0	0	A_1	1498	2	123	119	B_{3u}	688	4	0	A_1	688	2	309
36	B_{3g}	1500	0	67	B_2	1498	2	25	120	A_u	683	0	0	B_1	681	3	1
37	B_{1u}	1489	60	0	A_1	1483	94	566	121	B_{2g}	638	0	0	A_2	642	0	0
38	A_g	1476	0	1906	B_2	1481	80	25	122	B_{2u}	632	5	0	B_2	637	16	1
39	B_{2u}	1468	102	0	B_2	1475	9	1396	123	B_{1u}	632	54	0	B_1	633	0	0
40	B_{3g}	1466	0	637	A_1	1457	1	226	124	B_{1g}	629	0	0	A_1	625	5	79
41	A_g	1457	0	334	B_2	1440	48	646	125	A_u	618	0	0	B_2	618	1	0
42	B_{1u}	1430	31	0	A_1	1433	5	1478	126	B_{3g}	612	0	1	A_2	608	0	0
43	A_g	1426	0	570	A_1	1420	3	385	127	B_{3g}	580	0	2	B_2	584	5	0
44	A_g	1379	0	2622	B_2	1383	2	1627	128	A_g	577	0	45	A_1	576	2	29
45	B_{2u}	1376	127	0	A_1	1376	79	2026	129	B_{1u}	567	3	0	A_1	564	2	15
46	A_g	1367	0	2814	A_1	1370	35	759	130	B_{2u}	560	0	0	B_2	563	0	4
47	B_{1u}	1365	191	0	B_2	1366	195	20	131	A_g	551	0	34	B_2	546	2	33
48	B_{2u}	1346	126	0	B_2	1348	8	211	132	A_u	525	0	0	B_1	524	0	0
49	B_{1u}	1341	16	0	A_1	1344	175	1244	133	B_{1u}	502	6	0	B_2	507	5	3
50	B_{3g}	1334	0	340	A_1	1338	1	1023	134	B_{2u}	499	2	0	B_1	497	0	0
51	A_g	1332	0	6068	B_2	1333	41	243	135	B_{2g}	499	0	0	A_2	496	0	0
52	B_{2u}	1329	26	0	B_2	1327	77	4944	136	B_{1g}	498	0	0	A_1	494	4	9
53	B_{3g}	1317	0	174	A_1	1320	5	365	137	B_{3g}	487	0	136	A_1	487	2	97
54	B_{1u}	1307	47	0	A_1	1310	22	95	138	B_{3u}	442	14	0	B_1	441	14	0
55	B_{2u}	1288	22	0	B_2	1307	41	59	139	A_u	429	0	0	A_2	431	0	0

56	B_{3g}	1259	0	53	B_2	1297	8	812	140	B_{3u}	428	0	0	B_1	426	0	0
57	B_{3g}	1225	0	637	A_1	1234	10	782	141	B_{1g}	427	0	0	A_2	425	0	0
58	B_{2u}	1214	33	0	B_2	1226	4	241	142	B_{2g}	427	0	0	A_2	424	0	0
59	B_{3g}	1212	0	154	A_1	1205	2	95	143	B_{3u}	337	2	0	B_1	334	3	0
60	B_{1u}	1209	0	0	B_2	1200	1	555	144	B_{1u}	283	0	0	A_1	285	3	2
61	A_g	1205	0	1091	B_2	1193	2	164	145	B_{1g}	281	0	0	B_2	280	3	3
62	B_{1u}	1184	20	0	A_1	1191	38	126	146	B_{2u}	275	0	0	A_2	271	0	0
63	A_g	1184	0	362	A_1	1182	3	286	147	B_{2g}	266	0	0	B_1	268	0	0
64	B_{2u}	1181	6	0	B_2	1182	3	155	148	B_{3u}	256	2	0	A_2	249	0	0
65	A_g	1163	0	2282	B_2	1163	1	1836	149	B_{1g}	232	0	2	B_1	236	2	3
66	B_{2u}	1139	138	0	A_1	1144	101	676	150	A_g	230	0	74	A_1	230	1	63
67	A_g	1138	0	1085	A_1	1136	11	902	151	B_{2g}	223	0	3	A_2	218	0	3
68	B_{3g}	1133	0	359	B_2	1133	57	68	152	B_{3u}	217	7	0	B_1	217	2	0
69	B_{1u}	1131	72	0	A_1	1131	39	197	153	A_u	216	0	0	B_1	214	4	0
70	B_{3g}	1122	0	18	B_2	1118	3	41	154	B_{3g}	211	0	1	B_2	210	0	0
71	B_{2u}	1111	200	0	B_2	1114	26	43	155	B_{3g}	181	0	29	A_1	206	1	31
72	B_{3g}	1105	0	44	A_1	1109	100	1718	156	B_{3u}	134	0	0	A_2	133	0	0
73	B_{1u}	1086	12	0	B_2	1078	24	56	157	A_g	133	0	33	B_2	124	5	0
74	B_{2u}	1066	21	0	A_1	1074	6	17	158	B_{1g}	125	0	6	A_2	123	0	2
75	B_{3g}	1046	0	207	B_2	1053	372	1	159	B_{1u}	123	5	0	A_1	120	3	3
76	B_{1u}	1046	636	0	A_1	1051	12	160	160	B_{2u}	121	4	0	B_2	120	0	35
77	A_g	1029	0	539	A_1	1029	1	420	161	A_u	121	0	0	B_1	120	0	6
78	B_{2u}	1029	11	0	B_2	1028	4	30	162	B_{2g}	116	0	5	A_2	117	0	3
79	A_g	1029	0	215	A_1	1028	11	86	163	B_{3g}	84	0	5	A_1	104	0	10
80	B_{1u}	1029	0	0	B_2	1027	6	158	164	B_{1g}	57	0	0	B_1	64	0	0
81	B_{1g}	998	0	0	B_1	998	0	0	165	B_{2g}	55	0	0	B_1	53	0	0
82	A_u	998	0	0	A_2	998	0	0	166	A_u	52	0	0	A_2	50	0	0
83	B_{2g}	994	0	0	B_1	995	0	0	167	B_{3u}	38	2	0	B_1	39	2	0
84	A_u	994	0	0	A_2	995	0	0	168	B_{3u}	20	0	0	A_2	19	0	0