



SUPPLEMENTARY MATERIAL TO

Theoretical and experimental investigations on the structure and vibrational spectra of 6-amino-3-methyl-1-phenyl-1H-pyrazolo[3,4-*b*]pyridine-5-carboxylic acid and 6,7-dihydro-3-methyl-6-oxo-1-phenyl-1H-pyrazolo[3,4-*b*]pyridine-5-carbonitrile

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TABLE V-SM. Comparison of the observed and calculated frequencies (in cm^{-1}) of the fundamental vibrations of 6-amino-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylic acid (PYRPCA) and 6,7-dihydro-3-methyl-6-oxo-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile (PYRPCN) obtained by DFT force fields by B3LYP/6-31G*

No. <i>i</i>	IR	Raman	No scaling	Scaling ^a	Ai, IR ^b	Ii, Raman	PED %	IR	Raman	No scaling	Scaling ^a	Ai, IR ^b	Ii, Raman	PED %
1	3407	3413	3711	3559	62.78	203.60	OH(98)	3435	–	3593	3436	56.38	50.46	N1H(100)
2	3337	3339	3702	3551	123.89	83.69	NHs(92)	3088	3079	3237	3095	0.64	120.76	CH _{at} (99)
3	3301	3311	3552	3408	175.57	164.02	NHs(92)	3073	3065	3218	3077	15.36	203.77	CH _{at} (99)
4	3141	–	3263	3130	8.07	60.67	CH _{at} (90)	–	–	3211	3071	3.597	69.70	CH _{at} (99)
5	3114	–	3254	3122	6.81	62.34	CH _{at} (99)	–	–	3208	3068	19.17	68.21	CH _{at} (99)
6	–	–	3231	3100	0.45	107.67	CH _{at} (99)	–	–	3200	3060	4.71	106.00	CH _{at} (99)
7	3078	3072	3208	3077	38.41	215.86	CH _{at} (99)	–	–	3193	3053	2.31	26.55	CH _{at} (100)
8	–	–	3191	3062	24.55	139.59	CH _{at} (99)	3047	3047	3154	3016	5.90	82.58	CH3ops(72), CH3asym(23)
9	–	–	3182	3053	0.71	56.59	CH _{at} (99)	3022	3017	3105	2969	11.97	81.58	CH3ips(75), CH3ops(25)
10	3045	3042	3149	3044	7.39	80.79	CH3ips(95)	2920	2921	3052	2918	18.59	150.16	CH3ss(95)
11	3027	3031	3098	3030	15.64	92.02	CH3ops(100)	2226	2224	2347	2227	48.21	476.72	CN*(87), CC*(12)
12	2921	2926	3047	2923	26.08	206.86	CH3ss(94)	1655	1665	1792	1658	527.63	26.32	CO(66), CC _{at} (11)
13	1697	1699	1777	1721	416.13	190.17	CO(65), CC _{at} (8), bCO(10)	1616	1605	1663	1606	81.38	153.91	CC _{at} (47), CO(19), CN(13)
14	1654	1648	1677	1650	527.77	525.65	CC _{at} (46), bCH _{at} (16), CN(12)	1595	1592	1657	1601	171.96	81.97	CC _{at} (49), bCHar(20), CN(14)
15	1614	1633	1660	1638	236.71	4.15	CC _{at} (62), bCH _{at} (20)	–	–	1645	1589	103.48	12.71	CC _{at} (60), bCH _{at} (22)
16	–	–	1652	1626	220.66	6.70	CC _{at} (77), bCH _{at} (17)	1567	1565	1613	1564	288.66	19.63	CN(35), CC _{at} (34), bN1H(8)
17	1597	1596	1646	1602	29.19	80.07	bNHs(46), CN(H2)(24), CC _{at} (16)	1536	1535	1587	1531	55.14	303.41	CC _{at} (41), CO(31), bCH _{at} (13)

TABLE V-SM. Continued

No.i	IR	Raman	No scaling	Scaling ^a	Ai, IR ^b	Ii, Raman	PED %	IR	Raman	No scaling	Scaling ^a	Ai, IR ^b	Ii, Raman	PED %
18	1562	1563	1600	1565	144.34	30.31	CN(37), CCar(25), bNH(14)	1500	1494	1547	1504	114.90	39.29	bCH _{at} (57), CC _{at} (26), CN(13)
19	–	1525	1582	1531	23.46	135.59	CN(59), CCH ₃ (19), R1b(11)	1481	1479	1530	1477	15.37	6.56	CN(33), CC _{at} (17), CH ₃ opb(12), CCH ₃ (10)
20	1516	1509	1548	1516	200.26	50.46	bCH(54), CC _{at} (20), CN(15)	1461	–	1510	1462	7.97	34.40	bCH _{at} (57), CC _{at} (35)
21	1497	1493	1525	1491	16.15	2.66	CCar(45), bCH(19), bNH(15)	1455	–	1507	1449	12.70	19.76	CH3opb(36), CC _{at} (19), CH ₃ ipb(16), CCH ₃ (13)
22	1461	1471	1509	1478	8.64	22.48	bCH(35), CC _{at} (34)	1446	–	1503	1445	13.35	4.26	CH ₃ ipb(72), CH ₃ opb(28)
23	–	1455	1509	1446	37.63	43.02	CH ₃ ipb(80)	1429	–	1474	1422	36.36	44.26	CN(25), CH ₃ opb(21), CC _{at} (21), R1b(11)
24	1432	1432	1504	1444	18.57	93.28	CH ₃ opb(100)	1378	1381	1438	1378	4.13	15.23	CH ₃ sb(86)
25	–	–	1462	1425	117.18	220.96	CC _{at} (45), CN(19), CN(H ₂)(12)	–	–	1406	1353	11.37	39.88	CN(32), bN1H(29), CH _{at} (18), CC _{at} (14)
26	1429	1419	1458	1421	53.76	27.61	CN(49), CC _{at} (21), CN(H ₂)(11)	1339	1339	1369	1330	28.93	4.76	bCH _{at} (63), CC _{at} (16)
27	1382	1386	1432	1377	131.43	52.87	bOH(59), CC _{at} (26), CN(17)	1308	1304	1364	1319	18.23	3.58	CC _{at} (51), bCH _{at} (26)
28	1372	1362	1410	1372	68.53	22.71	CN(51), CC _{at} (24)	–	–	1345	1299	23.23	141.67	CC _{at} (68), bCH _{at} (21)
29	1354	1356	1390	1354	47.14	23.73	CH3sb(65), CN(14)	1270	1264	1322	1280	22.63	8.66	bCH _{at} (31), CC _{at} (30), bN1H(23)

TABLE V-SM. Continued

No.i	IR	Raman	No scaling	Scaling ^a	Ai, IR ^b	Ii, Raman	PED %	IR	Raman	No scaling	Scaling ^a	Ai, IR ^b	Ii, Raman	PED %
30	1342	1342	1373	1348	144.83	119.64	CC _{at} (72), bCH(23)	1241	–	1278	1232	11.44	5.85	bNIH(27), CC _{at} (17), CN(12), CC*(11)
31	1338	1339	1371	1338	12.43	33.27	bCH _{at} (30), CN(15), 1186	1186	1199	1220	1182	15.31	29.36	bCH _{at} (43), CN(19), CC _{at} (19)
32	–	–	1354	1331	0.58	37.21	CC _{at} (13), bOH(11), bCH _{at} (53), CC _{at} (19), bCNi(11)	–	1179	1207	1172	1.43	6.47	bCH _{at} (70), CC _{at} (16)
33	1306	1303	1324	1296	16.77	49.22	bCH _{at} (41), CC _{at} (25), CN(H ₂)(10)	1161	1156	1195	1162	0.10	2.13	bCH _{at} (83), CC _{at} (17)
34	1237	1232	1239	1211	20.18	71.22	CN(28), bCH _{at} (25), 1094	1094	1091	1188	1095	7.18	45.86	CN(36), bCO(14), CC _{at} (13), R2trigd(13)
35	–	1216	1215	1190	83.96	59.49	bCH _{at} (67), CC _{at} (14)	–	–	1125	1092	8.06	22.31	bCH _{at} (51), CC _{at} (32), NN(11)
36	–	1186	1208	1182	426.59	34.98	CC*(45), bCH(19), 1058	1058	1064	1098	1053	7.51	11.54	NN(36), CN(18), CC _{at} (16), bCH _{at} (15)
37	–	1172	1193	1166	0.97	9.41	CO(12), bCH _{at} (90)	–	1051	1079	1046	21.83	0.88	CC _{at} (30), bCH _{at} (18), CN(11), CC*(11), NN(10)
38	–	1159	1177	1147	14.14	47.37	CN(20), bNH(17), 1028	1028	1028	1075	1033	1.83	9.43	CH ₃ ipr(47), CH ₃ ipb(26), tR1(10), CH ₃ opb(9)
39	1103	1097	1123	1101	28.78	31.11	NN(17), bCH _{at} (16), bCH _{at} (54), CC _{at} (30)	–	–	1052	1023	12.79	1.09	CC _{at} (47), R3trig(20), bCH _{at} (19)

TABLE V-SM. Continued

No.i	IR	Raman	No scaling	Scaling ^a	Ai, IR ^b	Ii, Raman	PED %	IR	Raman	No scaling	Scaling ^a	Ai, IR ^b	Ii, Raman	PED %
40	1078	1073	1110	1081	46.73	16.16	R2trigd(31), bCH _{at} (13), CC _{at} (13)	1008	1001	1031	995	5.29	9.79	CC _{at} (47), R3trigd(20), bCH _{at} (19)
42	1049	1050	1074	1047	1.16	74.36	CC _{at} (50), bCH _{at} (28)	–	–	1001	982	0.18	0.31	gCH _{ar} (97)
43	–	1020	1064	1032	2.69	2.69	CH3ipr(45), CH3opb(43)	948	961	973	950	0.63	7.54	gCH _{at} (96)
44	1027	–	1050	1026	70.03	12.92	NH ₂ ipr (36), CO(24), CC _{at} (19)	–	945	959	934	9.24	42.09	gCH _{at} (94)
45	1016	–	1033	1008	16.15	8.21	R3trigd(58), CC _{at} (41)	911	907	932	908	5.35	1.93	gCH _{at} (80)
46	1000	100	1018	996	0.62	94.90	CN(47), CH ₃ ipb(25), bCN1(13)	–	–	924	900	1.48	3.08	gCH _{at} (26), CC _{at} (16), R1b(12), R2trig(12), CCH ₃ (10)
47	–	–	997	991	1.23	12.51	gCH _{at} (98)	854	848	857	829	27.73	3.41	gCH _{at} (54), CC _{at} (24)
48	–	971	977	970	0.02	0.97	gCH _{at} (93)	821	816	854	826	29.44	1.31	gCH _{at} (74), CC _{at} (10)
49	959	955	957	948	6.55	0.28	gCH _{at} (93)	764	753	778	759	38.98	5.69	gCO(62), gCC*(19), gNH(11)
50	916	–	930	922	6.04	1.03	gCH _{at} (86), gCN1(7)	752	733	769	750	24.68	1.46	gCH _{at} (76), gC12N(16)
51	–	900	919	903	1.33	1.03	R2trigd(19), CC _{at} (18), CCH ₃ (14), R1asym(13)	729	–	740	714	2.20	1.08	CC _{at} (37), gCH _{at} (21), R2trig(11), CN(10)
52	849	847	860	850	0.01	0.57	gCH _{at} (100)	692	676	735	689	1.97	18.63	gCC _{at} (42), rR1(20), gCCH ₃ (17), tR2asym(10)

TABLE V-SM. Continued

No.i	IR	Raman	No scaling	Scaling ^a	Ai, IR ^b	Ii, Raman	PED %	IR	Raman	No scaling	Scaling ^a	Ai, IR ^b	Ii, Raman	PED %
53	820	824	853	835	12.44	4.62	CC _{at} (29), R2asym(15), CN(8), CC*(7)	680	–	712	680	11.81	1.91	R3sym(40), R1b(18), CN(14), CC _{at} (12), bC C*(10)
54	796	792	799	766	42.15	3.01	gNH ₂ (52), gCC*(24), gNH ₂ (14)	668	662	694	663	19.23	1.87	gCH _{at} (30), gC12N(26), CC _{at} (12)
55	769	759	774	763	38.28	0.75	gCH _{at} (75), gCN1(19)	654	649	671	644	4.37	3.63	CH ₃ opr(33), gCH _{at} (27), gC12N(18)
56	746	743	764	744	2.74	0.14	bR1(43), gCC _{at} (12), tR2sym(11), tR2asym(10)	633	629	658	637	14.45	1.81	bCO(38), gCH _{at} (23), gC12N(18), bCC*(12), gN1H(10)
57	720	717	753	740	4.16	0.91	R2asym(57), CN(17), tCCO ₂ (11)	–	–	649	628	29.76	4.65	gN1H(54), gCC*(18), gCCH ₃ (10)
58	694	696	720	690	11.52	35.99	bCO ₂ (22), R2trigd(13), CC _{at} (11), CO ₂ (10)	–	608	628	618	15.26	3.31	R3asym(56), gN1H(34)
59	686	676	707	683	58.87	1.06	gCH _{at} (60), gCN1(37)	551	541	623	589	20.24	4.01	gCCH ₃ (30), tR1(26), gC12N(23), gN1H(19)
60	–	–	705	674	16.12	2.64	R3sym(34), R1trigd(13), CN(13), bCH _{at} (11)	–	–	556	532	3.84	1.41	bC12N(22), gCH _{at} (20), bCCH ₃ (13), tR3asym(10)
61	674	–	684	671	19.08	5.87	gCO ₂ (53), tR2asy(15), gCC*(10)	517	516	530	509	11.67	6.68	bCN'op(51), gCC*(20), gCO(18)

TABLE V-SM. Continued

No.i	IR	Raman	No scaling	Scaling ^a	Ai, IR ^b	Ii, Raman	PED %	IR	Raman	No scaling	Scaling ^a	Ai, IR ^b	Ii, Raman	PED %
62	–	–	657	644	61.94	1.19	bCO ₂ (27), bCNH ₂ (15), CCH ₃ (15), bCC*(11)	498	495	503	482	8.90	1.33	gC12N(24), tR3asym(20), bCCH3(11), gCH _{ar} (10)
63	651	651	653	633	2.60	0.19	CH ₃ opr(48), tCNH ₂ (17), tR1asym(15)	469	468	483	465	3.55	0.71	gC12N(21), bCO(13), tR3asym(13), gCH _{ar} (10)
64	626	623	644	625	2.65	1.26	tCNH ₂ (28), gCCH ₃ (18), tR1(16), gCN1(15)	448	–	466	452	7.37	8.25	gCH _{ar} (10), bCN'imp(31), R2asym(21), bCC*(8)
65	–	608	631	623	5.02	5.38	R3asym(66), bCN1(10)	403	418	425	395	1.17	0.52	gC12N(26), gCC*(22), gCCH ₃ (20)
66	–	–	624	611	12.21	1.22	bCO ₂ (35), R2sym(18), bCN1(13)	388	–	418	383	1.81	0.81	bCO(43), R2sym(22), bCN'imp(10)
67	553	522	588	541	106.19	6.29	t2R(85)	–	404	402	380	2.89	1.81	tR3asym(47), gCH _{ar} (39)
68	524	506	526	514	5.38	2.81	gCN1(41), tR3asym(28), gCH _{ar} (15)	370	–	394	376	7.08	1.66	gCC _{ar} (44), bCO(33), tR3asy(22)
69	515	486	510	503	7.40	2.37	R2asym(25), bCCH ₃ (18), bCN1(11)	–	320	317	304	1.60	2.26	bC12N(37), CN(34), bCO(10)
70	487	435	485	477	1.04	2.03	R2asym(38), bCN1(18), bCO ₂ (11)	–	302	299	289	0.35	3.41	CN(36), bC12N(25), R2sym(19)

TABLE V-SM. Continued

No.i	IR	Raman	No scaling	Scaling ^a	Ai, IR ^b	Ii, Raman	PED %	IR	Raman	No scaling	Scaling ^a	Ai, IR ^b	Ii, Raman	PED %
71	431	423	439	424	0.03	7.91	bCO ₂ (25), bCNH ₂ (23), bCN1(11), CC*(10)	–	267	267	257	1.54	2.06	gCC*(39), gCC _{at} (23), bCN'op(22)
72	421	415	431	423	3.56	2.28	gCC*(35), gNH ₂ (20), tR2sym(20)	–	248	239	225	1.55	2.34	tR3asym(37), bCCH ₃ (25), gCH _{at} (13)
73	–	390	417	403	0.04	4.41	tR3sym(61), gCH _{at} (19), tR3asym(19)	–	220	205	199	0.73	0.57	bCCH ₃ (53), tR3asym(23)
74	399	371	410	399	5.84	0.36	tCH ₃ (83)	–	159	204	192	1.21	0.48	gN1H(49), gCCH ₃ (30), tR(16)
75	–	326	387	380	3.38	1.33	bCNH ₂ (29), R2sym(16), CN(11)	–	133	134	129	2.77	4.73	bCC*(43), bCN'imp(35)
76	–	–	338	332	7.78	1.59	bCN1(30), CN(15), bCNH ₂ (12), bCC*(10)	–	121	121	114	2.72	0.33	tCH ₃ (30), gCC*(15), gN1H(13), gC12N(11)
77	–	294	310	306	17.28	1.39	gCC*(29), gCC _{at} (20), gCNH ₂ (15)	–	–	109	101	4.06	0.92	tCH ₃ (56), gN1H(18), gCC*(12)
78	–	280	287	282	1.77	3.82	bCN1(41), bCCH ₃ (17), CN(15)	–	–	92	86	0.18	0.25	gN1H(25), tR2asym(21), gC12N(20)
79	–	–	280	276	141.43	0.41	gCNH ₂ (48), tCNH ₂ (11), tR2sym(11)	–	–	76	72	1.35	5.60	bC12N(36), gC12N(22), tR2asym(14)

TABLE V-SM. Continued

No. <i>i</i>	IR	Raman	No scaling	Scaling ^a	Ai, IR ^b	Ii, Raman	PED %	IR	Raman	No scaling	Scaling ^a	Ai, IR ^b	Ii, Raman	PED %
80	–	221	239	234	0.52	4.66	bCC*(28), bCCH3(21), R2sym(11), CN(11)	–	–	51	47	0.28	2.45	tC12N(58), gC12N(14), bC12N(12)
81	–	197	232	226	3.10	0.51	tR3asym(49), gCCH3(18), gCH _{at} (13)	–	–	41	39	0.34	8.38	tC12N(40), gC12N(26)
82	–	165	205	199	48.48	4.62	gCNH ₂ (48), tR3asym(19), gCC*(11)							
83	–	131	178	175	0.36	0.51	bCCH3(34), bCC*(25), bCN1(17)							
84	–	–	132	128	0.01	4.62	gCC*(24), gCCH3(15), gCC _{at} (13)							
85	–	–	119	110	1.33	6.31	gCN1(21), tR3asym(16), tR2sym(11)							
86	–	–	104	103	0.37	0.76	bCN1(61), bCC*(15)							
87	–	–	88	86	0.36	0.66	gCN1(27), gCNH ₂ (25), tR2asym(22)							
88	–	–	68	63	5.46	1.26	gCNH ₂ (48), tCCO ₂ (44)							
89	–	–	39	38	1.56	0.35	tR2asym(22), gCNH ₂ (21), tR2sym(19), gCN1(15)							
90	–	–	8	8	0.15	2.83	tCN1(52), gCN1(15), gCNH ₂ (13), gCH _{at} (11)							

Abbreviations used: R, ring; ss, symmetric stretching; as, antisymmetric stretching; ips, in-plane stretching; ops, out-of-plane stretching; b, bending; ipb, in-plane bending; opb, out-of-plane bending; ipr, in-plane rock; opr, out-of-plane rock; asy, asymmetric; sym, symmetric; symd, symmetric deformation; asymd, antisymmetric deformation; g, wagging; t, torsion; trig, trigonal; trigd, trigonal deformation; ^aFor optimized values of the scale factors applied, see Tables III and IV; ^bRelative absorption intensities normalised with the highest peak absorbance