Supplementary Material (two pages) to

"NMR Crystallography of the Polymorphs of Metergoline"

by Czernek, Urbanová and Brus (*Crystals* 2018):

Results of the analysis of the HETCOR spectrum described in the main text; in Table 1 below, atoms are numbered as in the XRD structure **[reference 1]**;

δ is the experimental chemical shift as actually used;

σ is the GIPAW-RPBE chemical shielding as parsed from the CASTEP output;

ε is the theoretical chemical shift (in an ideal case, ε and δ would be the same for a given nucleus) **[references 2, 3]** approximated by entering a σ value into the corresponding model:

$\varepsilon(\mathrm{C}) = -0.978947*\sigma(\mathrm{C}) + 169.5016$ ppm; $\varepsilon(\mathrm{H}) = -1.01795*\sigma(\mathrm{H}) + 31.5801$ ppm;

the quantification of an level of agreement between theoretical and measured 2D spectra (which are expressed in terms of [ε(C); ε(H)] and [δ(C); δ(H)] pairs, respectively) leads to the following values of key statistical parameters **[references 2, 3]**:

$s_{\mathrm{C}} = 1.26$ ppm; $s_{\mathrm{H}} = 0.471$ ppm; $s_{\mathrm{CH}} = 0.125$ (ppm)^2

References

1. Hušák, M.; Jegorov, A.; Brus, J.; van Beek, W.; Pattison, P.; Christensen, M.; Favre-Nicolin, V.; Maixner, J. **2008**, *19*, 517.
2. Czernek, J.; Brus, J. *Chem. Phys. Lett.* **2014**, *586*, 56.
3. Czernek, J.; Brus, J. *Chem. Phys. Lett.* **2014**, *608*, 334.

Table 1

resolved $^{13}C - ^{1}H$ pair #	C in CIF	$\delta\ ^{13}C$ (ppm)	$\sigma\ ^{13}C$ (ppm)	$\varepsilon\ ^{13}C$ (ppm)	H in CIF	$\delta\ ^{1}H$ (ppm)	$\sigma\ ^{1}H$ (ppm)	$\varepsilon\ ^{1}H$ (ppm)
1	C101	121.41	51.8772	118.7166	H1011	6.09	24.5009	6.6393
2	C103	24.64	148.6116	24.0187	H1031	2.25	28.2562	2.8166
3	ditto	ditto	ditto	ditto	H1032	0.31	30.5250	0.5071
4	C104	67.23	106.1006	65.6348	H1041	1.87	28.9373	2.1233
5	C105	63.20	108.3439	63.4387	H1051	1.64	29.0951	1.9626
6	ditto	ditto	ditto	ditto	H1052	2.57	27.7577	3.3240
7	C106	37.73	134.5571	37.7774	H1061	2.24	28.9386	2.1219
8	C107	34.14	139.4236	33.0133	H1071	1.17	29.8190	1.2257
9	ditto	ditto	ditto	ditto	H1072	3.28	28.1017	2.9739
10	C108	38.92	133.2320	39.0746	H1081	1.21	30.0440	0.9967
11	C110	112.18	59.3606	111.3907	H1101	7.22	24.4351	6.7063
12	C111	119.98	50.2540	120.3056	H1111	6.77	24.9321	6.2004
13	C112	105.70	66.7012	104.2047	H1121	3.64	26.1867	4.9232
14	C117	46.27	125.5884	46.5572	H1171	3.75	27.7005	3.3823
15	ditto	ditto	ditto	ditto	H1172	ditto	26.8250	4.2735
16	C115	32.08	140.7491	31.7157	averaged: H1151–3	2.50	28.3791	2.6915
17	C116	43.48	128.8369	43.3771	averaged: H1161–3	2.57	28.4928	2.5757
18	C119	67.35	100.9125	70.7136	H1191	6.04	24.9636	6.1683
19	ditto	ditto	ditto	ditto	H1192	4.69	26.2504	4.8584
20	C123	126.32	42.5093	127.8873	H1231	7.41	23.6617	7.4936
21	C201	121.22	51.2631	119.3178	H2011	6.52	24.0662	7.0818
22	C203	24.75	147.2782	25.3241	H2031	0.22	30.9611	0.0631
23	ditto	ditto	ditto	ditto	H2032	3.12	29.0271	2.0318
24	C204	66.57	104.8818	66.8279	H2041	2.07	29.1581	1.8985
25	C205	62.28	110.2163	61.6057	H2051	2.57	28.6031	2.4635
26	ditto	ditto	110.2163	61.6057	H2052	1.99	28.9585	2.1017
27	C206	35.25	136.9671	35.4181	H2061	3.05	28.3934	2.6769
28	C207	31.19	142.9404	29.5705	H2071	2.70	28.6342	2.4318
29	ditto	ditto	ditto	ditto	H2072	2.13	29.0801	1.9779
30	C208	39.44	132.8446	39.4538	H2081	2.93	28.4761	2.5927
31	C210	121.22	59.0362	111.7083	H2101	6.52	24.8680	6.2656
32	C211	119.98	49.6622	120.8850	H2111	6.54	25.4018	5.7222
33	C212	105.26	65.5099	105.3709	H2121	5.46	25.0529	6.0774
34	C217	46.45	125.3728	46.7683	H2171	2.99	27.6303	3.4537
35	ditto	ditto	ditto	ditto	H2172	ditto	27.6346	3.4493
36	C215	34.25	138.0452	34.3627	averaged: H2151–3	4.43	26.9396	4.1568
37	C216	44.27	126.6297	45.5379	averaged: H2161–3	1.98	28.9853	2.0744
38	C219	68.21	101.7565	69.8874	H2191	4.87	26.5025	4.6018
39	ditto	ditto	ditto	ditto	H2192	5.25	25.9588	5.1552
40	C223	130.04	40.0567	130.2882	H2231	7.97	23.7541	7.3995