Supporting Information

Substituent effects on the energetic and aromaticity of aminomethylbenzoic acids

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Experimental Results

Table S1 – Calorimetric results for the calibration experiments with benzoic acid.

Benzoic acid (Calorimetric Standard NIST 39j)

	1	2	3	4	5	6	7	8	9	10	11
m(cpd.) / g	1.13642	0.80626	0.70474	0.66795	0.77120	0.80363	0.67539	0.75132	0.78391	0.59341	0.74475
m'(fuse) / g	0.00288	0.00228	0.00285	0.00344	0.00385	0.00219	0.00224	0.00220	0.00242	0.00284	0.00275
T_i / ºC	25.0000	25.0012	25.0005	25.0007	25.0006	25.0013	25.0004	25.0020	25.0011	25.0022	25.0021
T_f / ºC	26.9869	26.4474	26.2796	26.2135	26.3897	26.4431	26.2333	26.3583	26.2958	26.0988	26.3431
ΔT_{ad} / K	1.93365	1.37181	1.20071	1.13811	1.31478	1.36880	1.15052	1.27954	1.33435	1.01123	1.26752
ε_i (cont.) / J·K^{-1}	14.36	13.96	13.84	13.79	13.92	13.96	13.80	13.90	13.94	13.70	13.89
ε_f (cont.) / J·K^{-1}	15.59	14.83	14.60	14.52	14.75	14.83	14.53	14.71	14.78	14.35	14.69
Δm (H_2O) / g	-1.2	0.4	-0.7	0.3	-1.5	-3.1	-2.9	-3.5	-0.2	-1.9	0.6
-m(cpd.)·($\Delta_c U$) / J	30041.80	21312.77	18628.96	17656.41	20385.97	21243.19	17852.99	19860.27	20721.98	15685.69	19686.71
m'·$\Delta_c u^o$(fuse) / J	46.77	37.03	46.28	55.87	62.52	35.57	36.38	35.73	39.30	46.12	44.66
-ΔU(HNO_3) / J	11.74	8.15	7.23	5.47	8.09	8.15	7.44	7.52	8.35	5.71	7.69
-ΔU(ign) / J	1.20	1.21	1.18	1.19	1.19	1.16	1.13	1.17	1.14	1.06	1.05
-ΔU(carbon) / J	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ε(calor) / J·K^{-1}	15556.63	15553.55	15548.85	15552.97	15551.35	15550.50	15549.81	15556.06	15552.26	15557.40	15556.60

ε(calor) / J·K^{-1} = 15553.27 ± 0.91

Table S2 – Calorimetric results for 2-amino-3-methylbenzoic acid.

2-amino-3-methylbenzoic acid

	1	2	3	4	5	6	7
m(cpd.) / g	0.55130	0.53029	0.54810	0.49973	0.49432	0.52525	0.54655
m'(fuse) / g	0.00290	0.00248	0.00238	0.00272	0.00233	0.00228	0.00259
T_i / ºC	25.0008	25.0011	25.0372	25.0078	25.0004	25.0011	25.0013
T_f / ºC	26.0244	25.9920	26.0555	25.9470	25.9288	25.9856	26.0231
ΔT_{ad} / K	0.93944	0.90345	0.93337	0.85151	0.84136	0.89463	0.93124
ε_i (cont.) / J·K^{-1}	15.09	15.03	15.06	15.02	15.02	15.06	15.08
ε_f (cont.) / J·K^{-1}	15.57	15.53	15.57	15.49	15.47	15.53	15.61
Δm (H_2O) / g	-0.9	-2.4	-0.5	-2.0	0.4	-0.6	-2.3
-ΔU(IBP) / J	14622.45	14056.58	14529.63	13249.77	13100.37	13926.10	14489.42
$m'\cdot\Delta_c u^o$(fuse) / J	47.10	40.28	38.65	44.17	37.84	37.03	42.06
-ΔU(HNO_3) / J	28.24	24.06	24.42	22.98	22.92	25.31	23.40
-ΔU(ign) / J	1.20	1.20	1.20	1.21	1.20	1.20	1.20
-ΔU(carbon) / J	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ΔU_Σ / J	10.02	9.59	9.94	9.03	8.92	9.51	9.94
$\Delta_c u^0$ (cpd.) / J·g^{-1}	-26366.74	-26365.57	-26373.46	-26359.00	-26358.61	-26374.29	-26370.36

$\langle\Delta_c u^0\rangle$ / J·g^{-1} = -26366.9 ± 2.4

Table S3 – Calorimetric results for 2-amino-5-methylbenzoic acid.

2-amino-5-methylbenzoic acid

	1	2	3	4	5	6	7	8
m(cpd.) / g	0.54898	0.43564	0.49714	0.40011	0.42098	0.44374	0.48298	0.54996
m'(fuse) / g	0.00250	0.00268	0.00282	0.00259	0.00369	0.00255	0.00261	0.00263
T_i / °C	25.0008	25.0007	25.0003	25.0006	25.0010	25.0005	25.0011	25.0010
T_f / °C	26.0043	25.8174	25.9348	25.7795	25.8095	25.8456	25.9125	26.0237
ΔT_{ad} / K	0.93538	0.74276	0.84703	0.68183	0.71918	0.75559	0.82293	0.93715
ε_i (cont.) / J·K^{-1}	15.09	14.94	15.02	14.90	14.92	14.95	15.00	15.09
ε_f (cont.) / J·K^{-1}	15.57	15.33	15.48	15.27	15.31	15.37	15.43	15.58
Δm (H_2O) / g	-0.6	0.9	0.1	1.0	-1.3	4.3	-0.5	0.0
-ΔU(IBP) / J	14560.38	11566.55	13187.52	10617.87	11192.73	11777.10	12810.26	14590.38
$m'\cdot\Delta_c u^o$(fuse) / J	40.60	43.52	45.80	42.06	59.93	41.41	42.39	42.71
-ΔU(HNO_3) / J	27.46	21.73	23.34	18.09	19.52	19.88	23.70	26.98
-ΔU(ign) / J	1.19	1.19	1.20	1.20	1.20	1.19	1.19	1.20
-ΔU(carbon) / J	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ΔU_Σ / J	9.97	7.80	8.98	7.13	7.54	7.95	8.70	10.00
$\Delta_c u^0$ (cpd.) / J·g^{-1}	-26378.51	-26380.07	-26367.32	-26366.37	-26377.65	-26381.83	-26366.19	-26383.01

$\langle\Delta_c u^0\rangle$ / J·g^{-1} = -26375.1 ± 2.6

Table S4 – Calorimetric results for 2-amino-6-methylbenzoic acid.

2-amino-6-methylbenzoic acid

	1	2	3	4	5	6
m(cpd.) / g	0.49438	0.49987	0.51258	0.47646	0.43583	0.45215
m'(fuse) / g	0.00256	0.00307	0.00243	0.00308	0.00264	0.00245
T_i / °C	25.0014	25.0021	25.0009	25.0012	25.0010	25.0048
T_f / °C	25.9355	25.9477	25.9647	25.9066	25.8387	25.8688
ΔT_{ad} / K	0.84570	0.85508	0.87615	0.81577	0.74640	0.77421
ε_i (cont.) / J·K^{-1}	15.02	15.02	15.04	14.99	14.94	14.96
ε_f (cont.) / J·K^{-1}	15.47	15.49	15.51	15.44	15.34	15.37
Δm (H_2O) / g	-3.1	-1.5	-1.1	-2.7	-3.9	-4.4
-ΔU(IBP) / J	13155.55	13307.12	13636.52	12691.27	11608.29	12039.15
$m'\cdot\Delta_c u^o$(fuse) / J	41.57	49.86	39.46	50.02	42.87	39.79
-ΔU(HNO_3) / J	22.98	23.16	23.88	21.91	20.48	22.09
-ΔU(ign) / J	1.20	1.19	1.20	1.20	1.20	1.20
-ΔU(carbon) / J	0.00	0.00	0.00	0.00	0.00	0.00
ΔU_Σ / J	8.92	9.04	9.27	8.59	7.80	8.11
$\Delta_c u^0$ (cpd.) / J·g^{-1}	-26459.37	-26454.61	-26459.73	-26464.93	-26468.67	-26469.26

$\langle\Delta_c u^0\rangle$ / J·g^{-1} = −26462.8 ± 2.4

Table S5 – Calorimetric results for 3-amino-2-methylbenzoic acid.

3-amino-2-methylbenzoic acid

	1	2	3	4	5	6	7
m(cpd.) / g	0.49590	0.50666	0.49231	0.48554	0.47632	0.46526	0.51202
m'(fuse) / g	0.00291	0.00308	0.00315	0.00310	0.00301	0.00326	0.00259
T_i / ºC	25.0008	25.0006	25.0004	25.0009	25.0013	25.0006	25.0013
T_f / ºC	25.9347	25.9549	25.9299	25.9221	25.9033	25.8878	25.9446
ΔT_{ad} / K	0.84647	0.86607	0.84113	0.83246	0.81286	0.79824	0.87351
ε_i (cont.) / J·K^{-1}	15.02	15.03	15.02	15.01	14.99	14.98	15.04
ε_f (cont.) / J·K^{-1}	15.47	15.49	15.45	15.45	15.43	15.40	15.51
Δm (H_2O) / g	0.9	-3.0	-0.4	-12.7	2.5	-13.8	2.0
$-\Delta U(IBP)$ / J	13181.66	13472.72	13093.89	12916.05	12663.67	12381.49	13606.75
$m'\cdot\Delta_c u^o$(fuse) / J	47.26	50.02	51.16	50.34	48.88	52.94	42.06
$-\Delta U(HNO_3)$ / J	24.24	24.24	24.66	23.28	22.81	22.92	23.58
$-\Delta U$(ign) / J	1.20	1.19	1.19	1.19	1.20	1.20	1.19
$-\Delta U$(carbon) / J	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ΔU_Σ / J	8.95	9.17	8.89	8.76	8.58	8.37	9.26
$\Delta_c u^0$ (cpd.) / J·g^{-1}	-26416.79	-26424.00	-26422.14	-26429.31	-26415.27	-26428.07	-26426.09

$\langle\Delta_c u^0\rangle$ / J·g^{-1} = -26423.1 ± 2.0

Table S6 – Calorimetric results for 3-amino-4-methylbenzoic acid.

3-amino-4-methylbenzoic acid

	1	2	3	4	5	6
m(cpd.) / g	0.46807	0.70984	0.54449	0.51391	0.57391	0.54852
m'(fuse) / g	0.00265	0.00328	0.00286	0.00299	0.00310	0.00302
T_i / °C	25.0011	25.0015	25.0004	25.0005	25.0008	25.0005
T_f / °C	25.9330	26.2855	26.0142	25.9653	26.0630	26.0229
ΔT_{ad} / K	0.79766	1.20811	0.92850	0.87705	0.97821	0.93535
ε_i (cont.) / J·K^{-1}	14.98	15.29	15.08	15.04	15.12	15.09
ε_f (cont.) / J·K^{-1}	15.40	15.96	15.58	15.51	15.64	15.57
Δm (H_2O) / g	1.8	1.9	-2.8	-4.0	-1.5	-2.4
-ΔU(IBP) / J	12424.48	18819.00	14444.80	13639.91	15223.46	14552.96
$m'\cdot\Delta_c u^o$(fuse) / J	43.04	53.27	46.45	48.56	50.34	49.04
-ΔU(HNO_3) / J	22.94	32.20	26.09	24.84	27.82	28.18
-ΔU(ign) / J	1.19	1.19	1.20	1.19	1.19	1.19
-ΔU(carbon) / J	0.00	0.00	0.00	0.00	0.00	0.00
ΔU_Σ / J	8.42	13.20	9.90	9.30	10.47	9.97
$\Delta_c u^0$ (cpd.) / J·g^{-1}	-26382.75	-26370.89	-26375.36	-26378.21	-26369.20	-26369.95

$\langle\Delta_c u^0\rangle$ / J·g^{-1} = -26374.4 ± 2.2

Table S7 – Calorimetric results for 4-amino-3-methylbenzoic acid.

4-amino-3-methylbenzoic acid

	1	2	3	4	5	6
m(cpd.) / g	0.52826	0.49499	0.56732	0.50386	0.56581	0.57090
m'(fuse) / g	0.00273	0.00263	0.00270	0.00291	0.00338	0.00259
T_i / °C	25.0006	25.0009	25.0009	25.0009	25.0085	25.0010
T_f / °C	25.9851	25.9270	26.0455	25.9426	26.0506	26.0560
ΔT_{ad} / K	0.89837	0.84119	0.96423	0.85744	0.96262	0.97020
ε_i (cont.) / J·K^{-1}	15.06	15.02	15.11	15.03	15.11	15.12
ε_f (cont.) / J·K^{-1}	15.54	15.49	15.66	15.50	15.65	15.66
Δm (H_2O) / g	0.1	0.4	-0.2	-1.5	0.0	-1.6
-ΔU(IBP) / J	13986.97	13097.71	15011.19	13343.96	14986.94	15098.40
$m'\cdot\Delta_c u^o$(fuse) / J	44.34	42.71	43.85	47.26	54.89	42.06
-ΔU(HNO_3) / J	25.31	21.25	24.00	22.92	24.89	24.84
-ΔU(ign) / J	1.21	1.19	1.20	1.20	1.19	1.20
-ΔU(carbon) / J	0.00	0.00	0.00	0.00	0.00	0.00
ΔU_Σ / J	9.58	8.94	10.35	9.11	10.33	10.42
$\Delta_c u^0$ (cpd.) / J·g^{-1}	-26325.16	-26311.05	-26319.94	-26323.56	-26326.32	-26309.09

$\langle\Delta_c u^0\rangle$ / J·g^{-1} = -26319.2 ± 3.0

Computational results

Table S8 – NICS-scan values for the selected distances of the Bq atom from the centre of the averaged ring plane.

	NICS (ppm)			
Distance[a] / Å	Benzene	Aniline	Toluene	Benzoic acid
-2.0	-4.84	-4.02	-4.60	-4.85
-1.8	-5.84	-4.89	-5.56	-5.87
-1.6	-6.98	-5.91	-6.66	-7.03
-1.4	-8.20	-7.01	-7.83	-8.27
-1.2	-9.35	-8.07	-8.94	-9.44
-1.0	-10.22	-8.92	-9.79	-10.32
-0.8	-10.57	-9.36	-10.16	-10.65
-0.6	-10.25	-9.26	-9.90	-10.30
-0.4	-9.39	-8.72	-9.13	-9.40
-0.2	-8.45	-8.09	-8.29	-8.44
0.0	-8.04	-7.83	-7.95	-8.02
0.2	-8.45	-8.15	-8.36	-8.44
0.4	-9.39	-8.83	-9.24	-9.40
0.6	-10.25	-9.40	-10.03	-10.30
0.8	-10.57	-9.51	-10.30	-10.65
1.0	-10.22	-9.07	-9.93	-10.32
1.2	-9.35	-8.21	-9.07	-9.44
1.4	-8.20	-7.14	-7.96	-8.27
1.6	-6.98	-6.04	-6.78	-7.03
1.8	-5.84	-5.02	-5.68	-5.87
2.0	-4.84	-4.13	-4.71	-4.85

[a] The negative values refer to the side of the ring plane for where the amino lone pair points to and the positive values to the side for where the amino hydrogen's are oriented.

Table S8 – continued…

	NICS (ppm)				
Distance[a] / Å	2a-3m-BA	2a-4m-BA	2a-5m-BA	2a-6m-BA	3a-2m-BA
-2.0	-3.71	-3.41	-3.41	-3.45	-4.10
-1.8	-4.51	-4.14	-4.18	-4.17	-4.99
-1.6	-5.46	-5.00	-5.09	-5.00	-6.03
-1.4	-6.48	-5.93	-6.07	-5.90	-7.16
-1.2	-7.48	-6.82	-7.03	-6.76	-8.27
-1.0	-8.26	-7.52	-7.78	-7.43	-9.15
-0.8	-8.63	-7.84	-8.15	-7.73	-9.61
-0.6	-8.47	-7.69	-8.03	-7.57	-9.51
-0.4	-7.89	-7.16	-7.52	-7.03	-8.95
-0.2	-7.23	-6.58	-6.95	-6.43	-8.32
0.0	-6.95	-6.33	-6.71	-6.18	-8.08
0.2	-7.23	-6.60	-7.00	-6.45	-8.43
0.4	-7.89	-7.20	-7.60	-7.04	-9.12
0.6	-8.47	-7.74	-8.12	-7.57	-9.69
0.8	-8.62	-7.88	-8.22	-7.72	-9.79
1.0	-8.24	-7.54	-7.83	-7.41	-9.32
1.2	-7.46	-6.83	-7.05	-6.73	-8.43
1.4	-6.47	-5.93	-6.07	-5.87	-7.33
1.6	-5.44	-5.00	-5.07	-4.97	-6.19
1.8	-4.50	-4.14	-4.16	-4.13	-5.14
2.0	-3.70	-3.41	-3.40	-3.42	-4.24

[a] The negative values refer to the side of the ring plane for where the amino lone pair points to and the positive values to the side for where the amino hydrogen's are oriented.

Table S8 – continued…

	NICS (ppm)				
Distance[a] / Å	3a-4m-BA	3a-5m-BA	3a-6m-BA	4a-2m-BA	4a-3m-BA
-2.0	-3.94	-3.82	-3.99	-3.74	-3.94
-1.8	-4.83	-4.67	-4.89	-4.54	-4.88
-1.6	-5.87	-5.66	-5.94	-5.47	-5.99
-1.4	-7.02	-6.73	-7.09	-6.47	-7.20
-1.2	-8.15	-7.77	-8.20	-7.44	-8.37
-1.0	-9.05	-8.60	-9.10	-8.20	-9.28
-0.8	-9.52	-9.03	-9.58	-8.58	-9.68
-0.6	-9.42	-8.94	-9.50	-8.47	-9.46
-0.4	-8.84	-8.44	-8.97	-7.95	-8.74
-0.2	-8.17	-7.87	-8.35	-7.36	-7.96
0.0	-7.89	-7.68	-8.10	-7.13	-7.61
0.2	-8.22	-8.03	-8.42	-7.44	-7.94
0.4	-8.92	-8.71	-9.10	-8.09	-8.73
0.6	-9.52	-9.24	-9.67	-8.64	-9.47
0.8	-9.61	-9.30	-9.76	-8.74	-9.73
1.0	-9.13	-8.82	-9.29	-8.33	-9.35
1.2	-8.21	-7.94	-8.39	-7.54	-8.46
1.4	-7.08	-6.85	-7.27	-6.55	-7.30
1.6	-5.92	-5.75	-6.12	-5.53	-6.09
1.8	-4.87	-4.74	-5.06	-4.60	-4.98
2.0	-3.98	-3.89	-4.15	-3.80	-4.03

[a] The negative values refer to the side of the ring plane for where the amino lone pair points to and the positive values to the side for where the amino hydrogen’s are oriented.

S9 – Benzene (D6h)

Table S9.1 – Optimized geometry (Cartesian coordinates)

C	0	0.000000	1.394302	0.000000
C	0	1.207501	0.697151	0.000000
C	0	1.207501	-0.697151	0.000000
C	0	0.000000	-1.394302	0.000000
C	0	-1.207501	-0.697151	0.000000
C	0	-1.207501	0.697151	0.000000
H	0	0.000000	2.478593	0.000000
H	0	2.146524	1.239296	0.000000
H	0	2.146524	-1.239296	0.000000
H	0	0.000000	-2.478593	0.000000
H	0	-2.146524	-1.239296	0.000000
H	0	-2.146524	1.239296	0.000000

Table S9.2 – Calculated energies, in Hartree

E_0	$E_0 + \varepsilon_{ZPE}$	H (298.15 K)
-232.3113000	-232.2131796	-232.2076724

Scaled factors ZPE (0.9804) and *H*corr (0.9613) *T* =298.15K *P*= 1bar

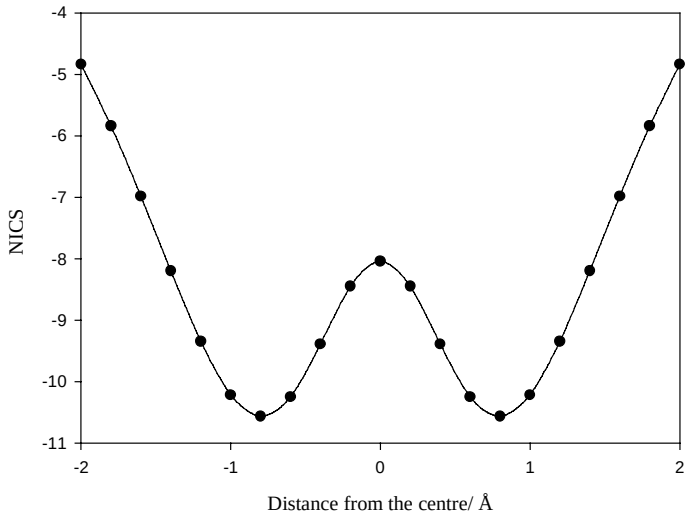

Figure S1 – NICS-scan plot for benzene

S10 - Aniline

Table S10.1 – Optimized geometry (Cartesian coordinates)

C	0	0.000000	0.000000	0.000000
C	0	0.000000	0.000000	1.391244
C	0	1.198169	0.000000	2.104854
C	0	2.401832	-0.000484	1.400547
C	0	2.412602	-0.000457	0.009355
C	0	1.209071	0.001317	-0.711576
N	0	1.214513	-0.055650	-2.108704
H	0	-0.940141	-0.005748	-0.542917
H	0	-0.946632	0.000686	1.920806
H	0	1.193974	0.000639	3.188208
H	0	3.344325	-0.000192	1.937451
H	0	3.356927	-0.006556	-0.526238
H	0	2.053713	0.282217	-2.556163
H	0	0.378965	0.282608	-2.562663

Table S10.2 – Calculated energies, in Hartree

E_0	$E_0 + \varepsilon_{ZPE}$	H (298.15 K)
-287.6877328	-287.5734952	-287.5664842

Scaled factors ZPE (0.9804) and *H*corr (0.9613) *T* =298.15K *P*= 1bar

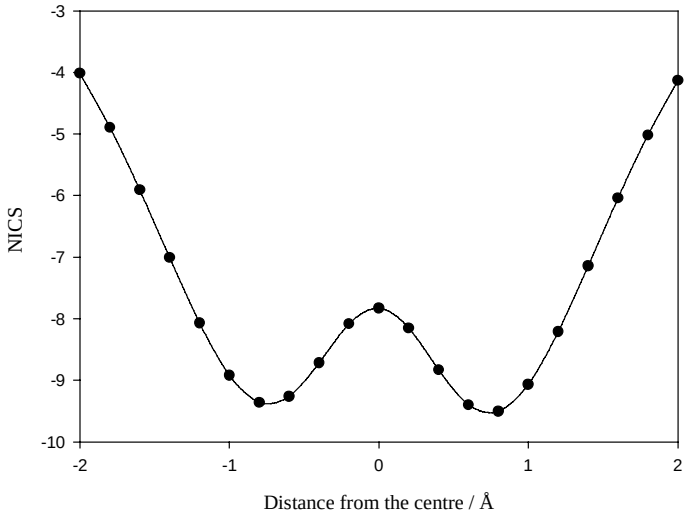

Figure S2 – NICS-scan plot for aniline

S11 - Toluene

Table S11.1 – Optimized geometry (Cartesian coordinates)

C	0	0.000000	0.000000	0.000000
C	0	0.000000	0.000000	1.393771
C	0	1.204937	0.000000	2.094428
C	0	2.406914	-0.001693	1.388771
C	0	2.401101	-0.001683	-0.005016
C	0	1.199057	0.002401	-0.721428
C	0	1.195874	0.035726	-2.231221
H	0	-0.944217	-0.004187	-0.535744
H	0	-0.941527	-0.004013	1.932158
H	0	1.207203	-0.002962	3.178577
H	0	3.350692	-0.007038	1.923197
H	0	3.343063	-0.007202	-0.544704
H	0	2.080354	-0.456024	-2.643006
H	0	0.311554	-0.459315	-2.639379
H	0	1.193167	1.067252	-2.600539

Table S11.2 – Calculated energies, in Hartree

E_0	$E_0 + \varepsilon_{ZPE}$	H (298.15 K)
-271.6388674	-271.5141201	-271.5067201

Scaled factors ZPE (0.9804) and *H*corr (0.9613) *T* =298.15K *P*= 1bar

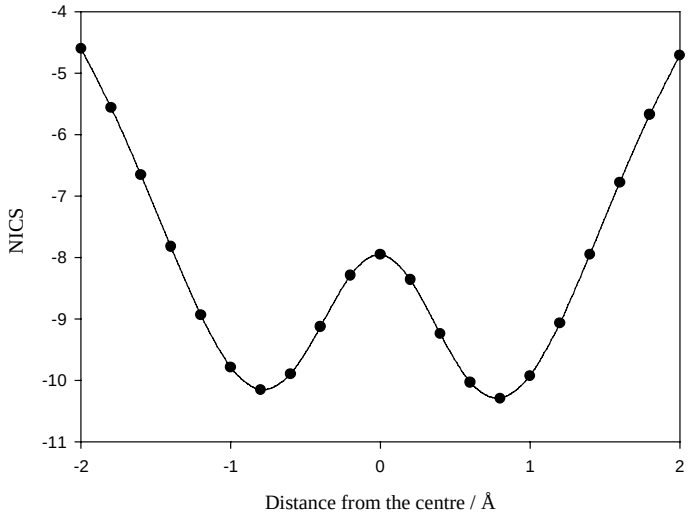

Figure S3 – NICS-scan plot for toluene

S12 - Benzoic acid

Table S12.1 – Optimized geometry (Cartesian coordinates)

C	0	0.000000	0.000000	0.000000
C	0	0.000000	0.000000	1.391825
C	0	1.206475	0.000000	2.091388
C	0	2.417941	0.000000	1.398653
C	0	2.423335	0.000000	0.008473
C	0	1.214283	0.000000	-0.696951
C	0	1.271780	0.000000	-2.182233
O	0	2.287322	0.000731	-2.838491
O	0	0.043137	-0.000948	-2.762017
H	0	-0.932495	0.000000	-0.548940
H	0	-0.940420	0.000000	1.930868
H	0	1.202947	0.000000	3.175748
H	0	3.355312	0.000000	1.942884
H	0	3.352162	0.000000	-0.548455
H	0	0.188049	-0.000823	-3.719447

Table S12.2 – Calculated energies, in Hartree

E_0	$E_0 + \varepsilon_{ZPE}$	H (298.15 K)
-420.9482584	-420.8353508	-420.8270278

Scaled factors ZPE (0.9804) and *H*corr (0.9613) *T* =298.15K *P*= 1bar

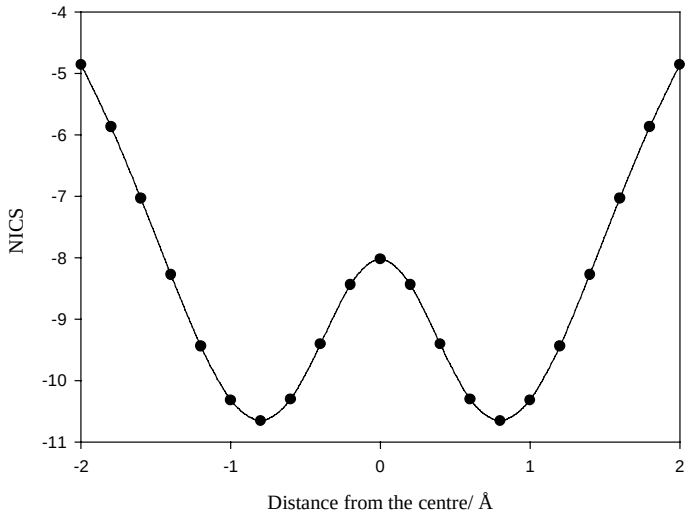

Figure S4 – NICS-scan plot for benzoic acid

S13 - 2-amino-3-methylbenzoic acid

Table S13.1 – Optimized geometry (Cartesian coordinates)

C	0	0.000000	0.000000	0.000000
C	0	0.000000	0.000000	1.385522
C	0	1.185553	0.000000	2.132493
C	0	2.394990	0.004340	1.467886
C	0	2.451393	0.008849	0.061025
C	0	1.242738	0.002254	-0.693588
C	0	3.749666	0.037953	-0.621096
O	0	3.929543	0.071332	-1.829919
O	0	4.815382	0.030719	0.222420
N	0	1.250727	-0.032953	-2.058595
C	0	-1.291037	-0.011613	-0.777954
H	0	-0.954464	-0.002863	1.902913
H	0	1.150986	-0.002720	3.214858
H	0	3.324520	0.007665	2.020702
H	0	5.603201	0.056018	-0.339460
H	0	0.400884	0.134529	-2.566954
H	0	2.138800	0.067806	-2.531696
H	0	-2.148430	-0.023318	-0.103825
H	0	-1.366453	-0.893172	-1.425397
H	0	-1.392533	0.873944	-1.417929

Table S13.2 – Calculated energies, in Hartree

E_0	$E_0 + \varepsilon_{ZPE}$	H (298.15 K)
-515.6586704	-515.5029089	-515.490935

Scaled factors ZPE (0.9804) and *H*corr (0.9613) *T* =298.15K *P*= 1bar

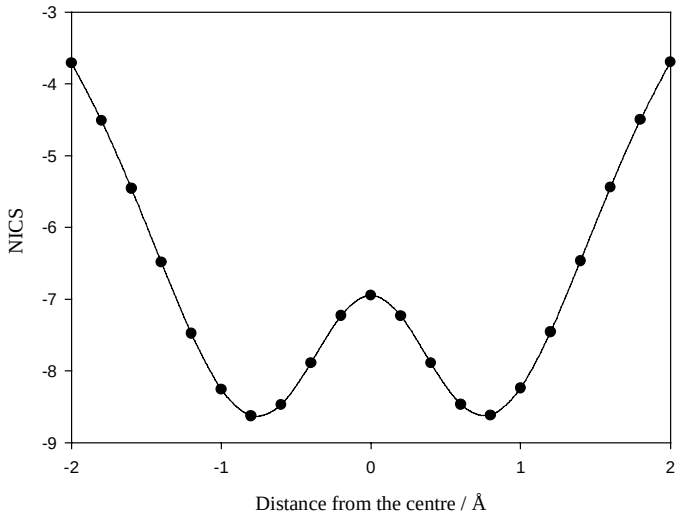

Figure S5 – NICS-scan plot for 2-amino-3-methylbenzoic acid

S14 - 2-amino-4-methylbenzoic acid

Table S14.1 – Optimized geometry (Cartesian coordinates)

C	0	0.000000	0.000000	0.000000
C	0	0.000000	0.000000	1.384203
C	0	1.232841	0.000000	2.068806
C	0	2.413749	0.004273	1.357410
C	0	2.432240	0.007394	-0.052009
C	0	1.194858	0.000302	-0.754919
C	0	3.699654	0.033646	-0.782398
O	0	3.828941	0.063914	-1.998081
O	0	4.799109	0.026706	0.018221
N	0	1.131241	-0.029505	-2.116372
C	0	-1.294501	-0.001613	2.157599
H	0	-0.944974	-0.005940	-0.535304
H	0	1.250020	-0.001431	3.152782
H	0	3.360840	0.008421	1.880526
H	0	5.563526	0.049676	-0.575020
H	0	0.245591	0.099877	-2.573855
H	0	1.988750	0.062568	-2.643378
H	0	-1.363216	0.878945	2.803801
H	0	-1.360281	-0.881748	2.804650
H	0	-2.160960	-0.003450	1.494016

Table S14.2 – Calculated energies, in Hartree

E_0	$E_0 + \varepsilon_{ZPE}$	H (298.15 K)
-515.6600664	-515.5041988	-515.4926298

Scaled factors ZPE (0.9804) and *H*corr (0.9613) *T* =298.15K *P*= 1bar

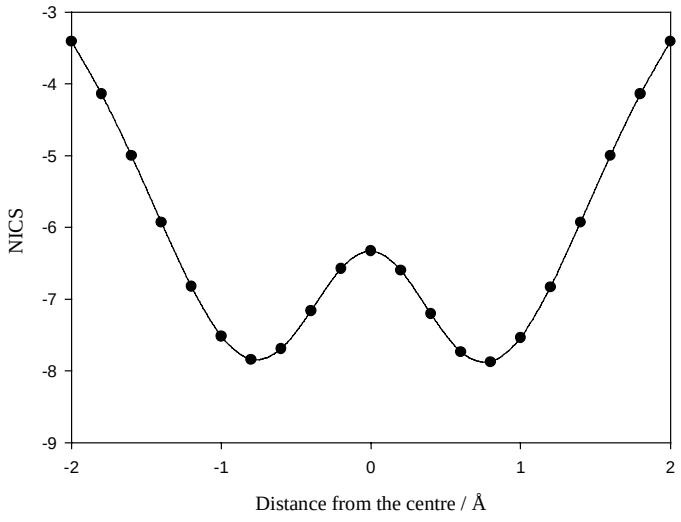

Figure S6 – NICS-scan plot for 2-amino-4-methylbenzoic acid

S15 - 2-amino-5-methylbenzoic acid

Table S15.1 – Optimized geometry (Cartesian coordinates)

C	0	0.000000	0.000000	0.000000
C	0	0.000000	0.000000	1.379459
C	0	1.195779	0.000000	2.123740
C	0	2.381917	-0.006028	1.411025
C	0	2.422486	-0.010604	0.000543
C	0	1.206562	-0.001570	-0.735368
C	0	3.708342	-0.043174	-0.702175
O	0	3.863165	-0.083088	-1.913954
O	0	4.790022	-0.031413	0.121582
N	0	1.169668	0.035050	-2.100246
C	0	1.169270	0.005345	3.633196
H	0	-0.940377	0.007186	-0.541835
H	0	-0.952091	0.001356	1.902172
H	0	3.325317	-0.011488	1.942004
H	0	5.566966	-0.060449	-0.454984
H	0	0.295607	-0.126235	-2.570301
H	0	2.035567	-0.083585	-2.607479
H	0	2.180506	-0.010750	4.044639
H	0	0.635719	-0.865461	4.027790
H	0	0.666624	0.897017	4.021988

Table S15.2 – Calculated energies, in Hartree

E_0	$E_0 + \varepsilon_{ZPE}$	H (298.15 K)
-515.6580783	-515.5017406	-515.4905636

Scaled factors ZPE (0.9804) and *H*corr (0.9613) *T* =298.15K *P*= 1bar

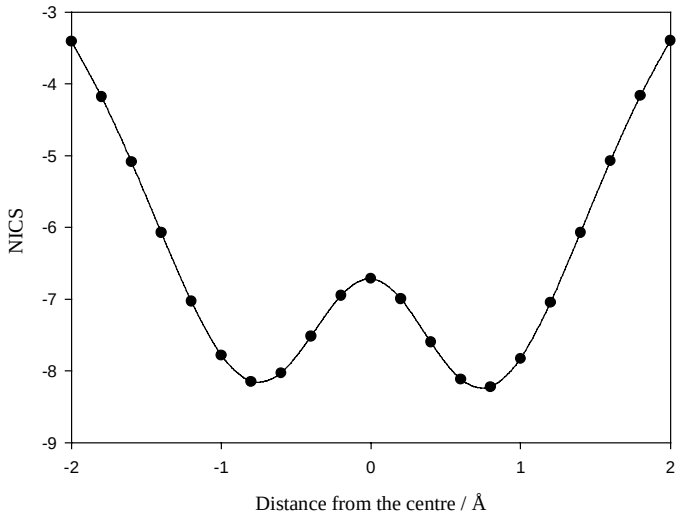

Figure S7 – NICS-scan plot for 2-amino-5-methylbenzoic acid

S16 - 2-amino-6-methylbenzoic acid

Table S16.1 – Optimized geometry (Cartesian coordinates)

C	0	0.000000	0.000000	0.000000
C	0	0.000000	0.000000	1.375374
C	0	1.203996	0.000000	2.086156
C	0	2.429304	-0.002122	1.430123
C	0	2.454929	-0.003479	0.000054
C	0	1.214068	-0.000629	-0.720878
C	0	3.695023	0.004427	-0.792554
O	0	3.762335	0.086752	-2.012672
O	0	4.850832	-0.093368	-0.086240
N	0	1.148014	-0.025003	-2.082377
C	0	3.663274	0.006181	2.305947
H	0	-0.933530	-0.002244	-0.552704
H	0	-0.942540	0.001835	1.912317
H	0	1.185589	0.004010	3.169109
H	0	5.558210	-0.070106	-0.747495
H	0	0.253726	0.089139	-2.527008
H	0	1.998854	0.081203	-2.616687
H	0	3.360886	0.039833	3.353593
H	0	4.303069	0.866543	2.103318
H	0	4.278030	-0.882043	2.151917

Table S16.2 – Calculated energies, in Hartree

E_0	$E_0 + \varepsilon_{ZPE}$	H (298.15 K)
-515.6513971	-515.4952715	-515.4837785

Scaled factors ZPE (0.9804) and *H*corr (0.9613) *T* =298.15K *P*= 1bar

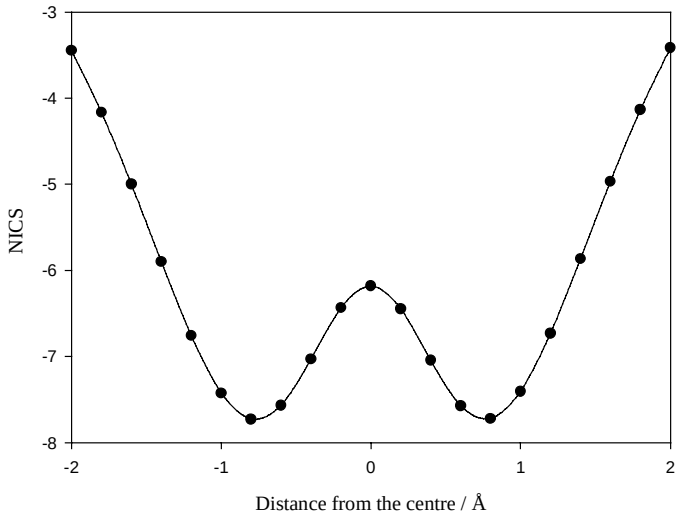

Figure S8 – NICS-scan plot for 2-amino-6-methylbenzoic acid

S17 - 3-amino-2-methylbenzoic acid

Table S17.1 – Optimized geometry (Cartesian coordinates)

C	0	0.000000	0.000000	0.000000
C	0	0.000000	0.000000	1.400100
C	0	1.193347	0.000000	2.109228
C	0	2.402983	0.010201	1.429884
C	0	2.420081	0.027215	0.026029
C	0	1.219905	0.004686	-0.715409
C	0	3.746344	0.117635	-0.648861
O	0	3.965997	0.534232	-1.764623
O	0	4.766567	-0.307200	0.146337
N	0	-1.215303	-0.066692	-0.688414
C	0	1.147810	-0.057507	-2.221578
H	0	-0.947787	-0.004538	1.929798
H	0	1.177807	-0.001834	3.192965
H	0	3.337348	0.019186	1.972268
H	0	5.579461	-0.166185	-0.360578
H	0	-2.029387	0.177068	-0.144074
H	0	-1.234257	0.348463	-1.607519
H	0	2.112770	-0.253435	-2.675726
H	0	0.791214	0.892885	-2.640209
H	0	0.443281	-0.837084	-2.529246

Table S17.2 – Calculated energies, in Hartree

E_0	$E_0 + \varepsilon_{ZPE}$	H (298.15 K)
-515.6464021	-515.4901204	-515.478688

Scaled factors ZPE (0.9804) and *H*corr (0.9613) *T* =298.15K *P*= 1bar

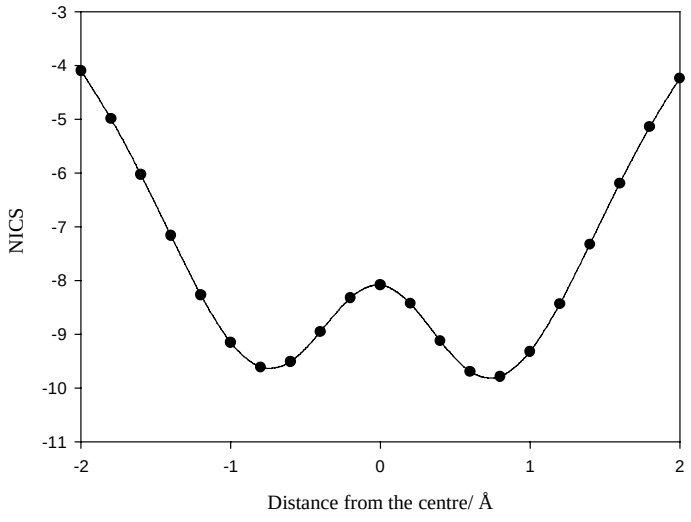

Figure S9 – NICS-scan plot for 3-amino-2-methylbenzoic acid

S18 - 3-amino-4-methylbenzoic acid

Table S18.1 – Optimized geometry (Cartesian coordinates)

C	0	0.000000	0.000000	0.000000
C	0	0.000000	0.000000	1.413604
C	0	1.225254	0.000000	2.082211
C	0	2.438648	-0.006824	1.402174
C	0	2.429796	-0.011571	0.004130
C	0	1.216521	-0.006353	-0.686168
C	0	3.679391	-0.015912	-0.796816
O	0	3.734694	-0.010228	-2.006057
O	0	4.803725	-0.026407	-0.032756
N	0	-1.204672	-0.057547	-0.705458
C	0	-1.300668	-0.009147	2.172162
H	0	1.224378	0.001610	3.167361
H	0	3.375501	-0.008710	1.941725
H	0	1.235281	-0.010084	-1.770282
H	0	5.552463	-0.028350	-0.646548
H	0	-2.011216	0.346603	-0.254012
H	0	-1.146963	0.192321	-1.681670
H	0	-1.126403	-0.045060	3.248328
H	0	-1.914754	-0.874479	1.899223
H	0	-1.898070	0.888733	1.968237

Table S18.2 – Calculated energies, in Hartree

E_0	$E_0 + \varepsilon_{ZPE}$	H (298.15 K)
-515.6535369	-515.4974480	-515.485950

Scaled factors ZPE (0.9804) and *H*corr (0.9613) *T* =298.15K *P*= 1bar

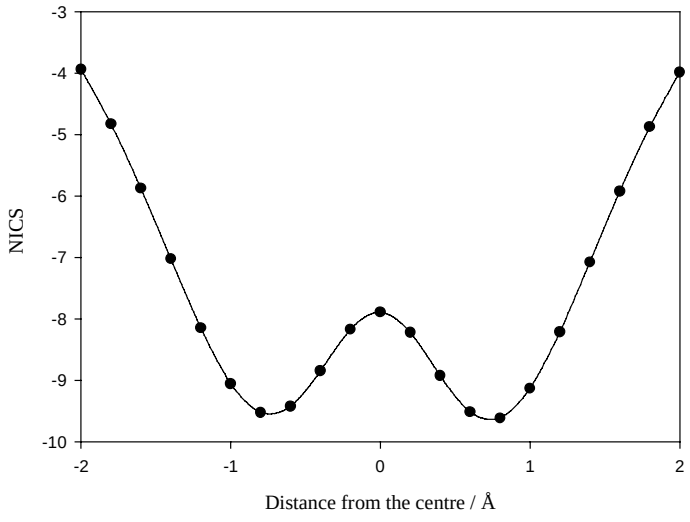

Figure S10 – NICS-scan plot for 3-amino-4-methylbenzoic acid

S19 - 3-amino-5-methylbenzoic acid

Table S19.1 – Optimized geometry (Cartesian coordinates)

C	0	0.000000	0.000000	0.000000
C	0	0.000000	0.000000	1.402279
C	0	1.188374	0.000000	2.136023
C	0	2.405733	0.002482	1.453016
C	0	2.418981	0.002275	0.053338
C	0	1.227621	-0.000003	-0.670957
C	0	3.689201	0.010339	-0.719584
O	0	3.771090	0.021710	-1.926842
O	0	4.796022	0.003980	0.068897
N	0	-1.199049	-0.056843	-0.711715
C	0	1.146904	-0.017956	3.645877
H	0	-0.950615	-0.004721	1.929067
H	0	3.339318	0.007115	1.999403
H	0	1.271399	-0.002405	-1.753833
H	0	5.558282	0.009442	-0.528080
H	0	-2.016746	0.286339	-0.230336
H	0	-1.156506	0.254028	-1.670825
H	0	2.134815	0.168164	4.070872
H	0	0.802095	-0.988461	4.017432
H	0	0.462766	0.741437	4.034721

Table S19.2 – Calculated energies, in Hartree

E_0	$E_0 + \varepsilon_{ZPE}$	H (298.15 K)
-515.6528972	-515.4972468	-515.485432

Scaled factors ZPE (0.9804) and *H*corr (0.9613) *T* =298.15K *P*= 1bar

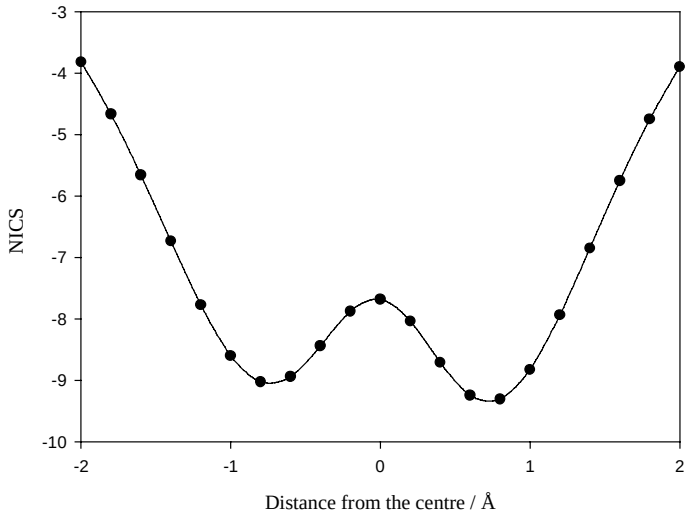

Figure S11 – NICS-scan plot for 3-amino-5-methylbenzoic acid

S20 - 3-amino-6-methylbenzoic acid

Table S20.1 – Optimized geometry (Cartesian coordinates)

C	0	0.000000	0.000000	0.000000
C	0	0.000000	0.000000	1.399250
C	0	1.167243	0.000000	2.151398
C	0	2.417823	0.003576	1.521123
C	0	2.444498	0.003822	0.125690
C	0	1.264667	0.002103	-0.631926
C	0	1.372754	0.003207	-2.114943
N	0	3.601126	-0.054703	2.263829
C	0	-1.320485	-0.000550	-0.731104
O	0	2.662745	0.025139	-2.557882
O	0	0.451963	-0.012873	-2.900774
H	0	-0.952784	-0.000540	1.917990
H	0	1.109345	-0.007098	3.235463
H	0	3.396052	0.000836	-0.390028
H	0	3.541639	0.297424	3.207942
H	0	4.430009	0.271495	1.788959
H	0	-2.140930	0.005748	-0.010180
H	0	-1.428204	-0.876641	-1.374052
H	0	-1.423924	0.868139	-1.384714
H	0	2.612978	0.019816	-3.524562

Table S20.2 – Calculated energies, in Hartree

E_0	$E_0 + \varepsilon_{ZPE}$	H (298.15 K)
-515.6482866	-515.4922844	-515.480737

Scaled factors ZPE (0.9804) and *H*corr (0.9613) *T* =298.15K *P*= 1bar

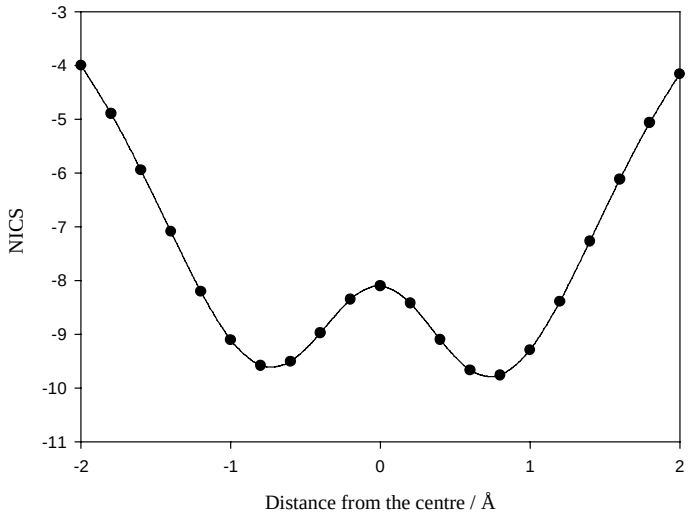

Figure S12 – NICS-scan plot for 3-amino-6-methylbenzoic acid

S21 - 4-amino-2-methylbenzoic acid

Table S21.1 – Optimized geometry (Cartesian coordinates)

C	0	0.000000	0.000000	0.000000
C	0	0.000000	0.000000	1.403541
C	0	1.233762	0.000000	2.073848
C	0	2.408122	0.002909	1.346301
C	0	2.412691	0.004371	-0.059795
C	0	1.173030	0.002678	-0.749463
C	0	3.697816	0.009848	-0.782837
O	0	3.854128	0.014308	-1.986474
O	0	4.781160	0.009658	0.051812
N	0	-1.190058	-0.049657	2.108034
C	0	1.058647	0.003849	-2.253933
H	0	-0.952340	-0.005594	-0.521537
H	0	1.262942	-0.005722	3.158303
H	0	3.354964	0.004770	1.869053
H	0	5.557879	0.012628	-0.525236
H	0	-1.167196	0.228668	3.076668
H	0	-2.029237	0.225548	1.622099
H	0	1.552282	-0.865870	-2.691725
H	0	1.547744	0.876658	-2.690688
H	0	0.007956	0.000962	-2.551039

Table S21.2 – Calculated energies, in Hartree

E_0	$E_0 + \varepsilon_{ZPE}$	H (298.15 K)
-515.6531944	-515.4970534	-515.485524

Scaled factors ZPE (0.9804) and *H*corr (0.9613) *T* =298.15K *P*= 1bar

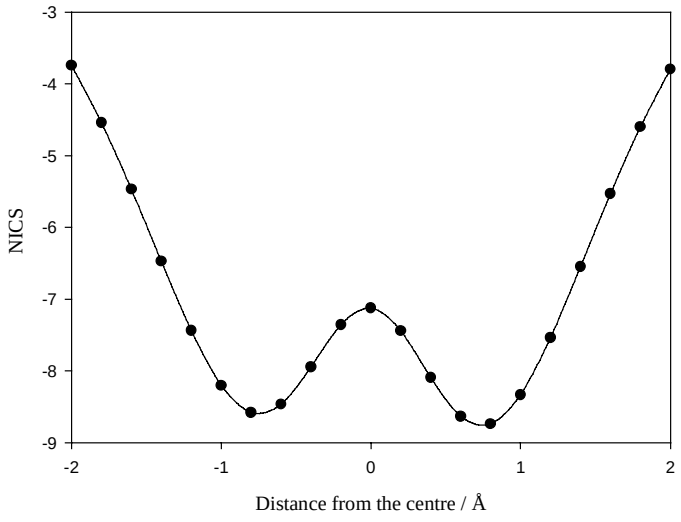

Figure S13 – NICS-scan plot for 4-amino-2-methylbenzoic acid

S22 - 4-amino-3-methylbenzoic acid

Table S22.1 – Optimized geometry (Cartesian coordinates)

C	0	0.000000	0.000000	0.000000
C	0	0.000000	0.000000	1.384340
C	0	1.205779	0.000000	2.106068
C	0	2.437972	-0.003428	1.408452
C	0	2.411821	-0.000910	0.020981
C	0	1.211516	0.001160	-0.702462
C	0	1.277241	0.005061	-2.175343
O	0	2.293624	0.007859	-2.836186
O	0	0.048714	0.005607	-2.767449
N	0	1.185845	-0.049558	3.490838
C	0	3.741943	-0.017067	2.164976
H	0	-0.936610	0.001400	-0.541878
H	0	-0.941141	-0.002612	1.925054
H	0	3.343124	-0.001859	-0.533894
H	0	0.208383	0.007740	-3.722038
H	0	2.006154	0.263610	3.984920
H	0	0.319398	0.194576	3.944690
H	0	3.818748	-0.892054	2.820240
H	0	3.860369	0.874301	2.794281
H	0	4.588046	-0.040941	1.477309

Table S22.2 – Calculated energies, in Hartree

E_0	$E_0 + \varepsilon_{ZPE}$	H (298.15 K)
-515.6562905	-515.4999259	-515.488428

Scaled factors ZPE (0.9804) and *H*corr (0.9613) *T* =298.15K *P*= 1bar

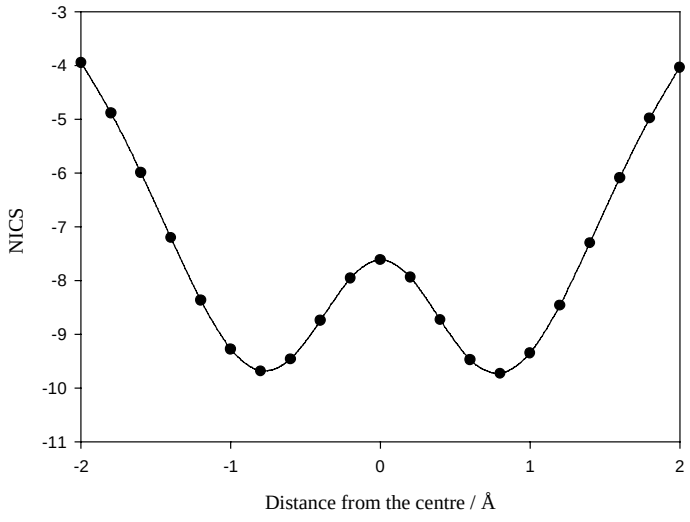

Figure S14 – NICS-scan plot for 4-amino-3-methylbenzoic acid