Supplementary material for the article:

Baranac-Stojanović, M. Can Variations of 1H NMR Chemical Shifts in Benzene Substituted with an Electron-Accepting (NO2)/Donating (NH2) Group Be Explained in Terms of Resonance Effects of Substituents? *Chemistry - An Asian Journal* **2018**, *13* (7), 877–881. https://doi.org/10.1002/asia.201800137

CHEMISTRY
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Supporting Information

Can Variations of ^{1}H NMR Chemical Shifts in Benzene Substituted with an Electron-Accepting (NO_2)/Donating (NH_2) Group be Explained in Terms of Resonance Effects of Substituents?

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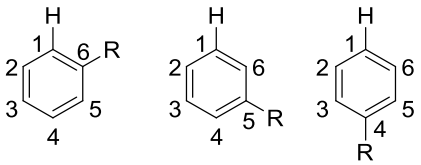
Table S1. Experimental (in $CDCl_3$)[1,2] and calculated (BPW91/6-311G(d,p)//BPW91/6-311++G(d,p), in $CHCl_3$) ^1H NMR chemical shifts of benzene (R = H), aniline (R = NH_2) and nitrobenzene (R = NO_2) in *ortho* (*o*-), *meta* (*m*-) and *para* (*p*-) relation to the substituent.

R	H	*o*-NH_2	*m*-NH_2	*p*-NH_2	*o*-NO_2	*m*-NO_2	*p*-NO_2
Exp	7.31	6.68	7.15	6.76	8.16	7.52	7.68
Calc	7.57	6.66	7.21	6.70	8.38	7.75	7.91

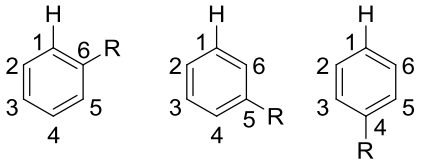
Table S2. NLMO contributions to the total isotropic proton shielding in benzene (R = H), aniline (R = NH_2) and nitrobenzene (R = NO_2), calculated at the BPW91/6-311G(d,p)//BPW91/6-311++G(d,p), in $CHCl_3$. The proton in question is the one bound to the C1 atom. Values are in ppm.



NLMO	H	*o*-NH_2	*m*-NH_2	*p*-NH_2	*o*-NO_2	*m*-NO_2	*p*-NO_2
C1-C2	-2.13	-1.83	-2.38	-2.05	-2.01	-2.60	-2.62
C1-C6	-2.13	-1.61	-2.22	-2.05	-1.64	-2.19	-2.62
C2-C3	-0.33	-0.35	-0.25	-0.36	-0.22	-0.24	-0.37
C5-C6	-0.33	-0.26	-0.31	-0.36	-0.29	-0.33	-0.37
C3-C4	-0.04	-0.01	-0.06	-0.05	0.05	-0.07	-0.11
C4-C5	-0.04	0.01	-0.06	-0.05	-0.02	-0.11	-0.11
C-C$_{total}$	**-5.00**	**-4.05**	**-5.28**	**-4.92**	**-4.13**	**-5.54**	**-6.18**
C1-H	27.10	26.84	27.17	27.08	26.14	26.97	27.14
C2-H	-0.27	-0.30	-0.21	-0.24	-0.33	-0.26	-0.18
C6-H	-0.27	/	-0.23	-0.24	/	-0.21	-0.18
C3-H	-0.06	-0.06	-0.08	-0.07	-0.08	-0.06	-0.03
C5-H	-0.06	-0.04	/	-0.07	-0.05	/	-0.03
C4-H	-0.09	-0.08	-0.07	/	-0.09	-0.05	/
C-H$_{total}$	**26.35**	**26.36**	**26.58**	**26.46**	**25.59**	**26.39**	**26.72**
C=C$_{total}$	**2.27**	**2.35**	**2.66**	**2.89**	**2.05**	**2.40**	**2.28**

CR (C)$_{total}$	**0.47**	**0.40**	**0.60**	**0.61**	**0.26**	**0.72**	**0.98**
C-N	/	-0.50	-0.19	-0.17	-0.26	-0.02	-0.01
N-H$_{total}$	/	0.06	0.08	0.06	/	/	/
N-O$_{total}$	/	/	/	/	0.53	0.23	0.18
N=O	/	/	/	/	1.04	0.27	0.16
LP$_{\pi}$	/	0.41	0.00	0.05	-0.52	-0.19	-0.12
LP$_{other}$	/	/	/		-1.23	-0.30	-0.26
CR (N/O)$_{total}$	/	-0.04	-0.02	-0.02	-0.06	-0.02	-0.02
R	**/**	**-0.48**	**-0.13**	**-0.13**	**-1.02**	**-0.11**	**-0.09**
π_{total}	**2.27**	**2.76**	**2.65**	**2.94**	**2.57**	**2.48**	**2.32**
Total	**24.09**	**24.99**	**24.42**	**24.96**	**23.27**	**23.94**	**23.75**

Table S3. NLMO contributions to the paramagnetic and diamagnetic component of shielding tensor in benzene (R = H), aniline (R = NH_2) and nitrobenzene (R = NO_2), calculated at the BPW91/6-311G(d,p)//BPW91/6-311++G(d,p), in $CHCl_3$. The proton in question is the one bound to the C1 atom. Values are in ppm.



NLMO	H	*o*-NH_2	*m*-NH_2	*p*-NH_2	*o*-NO_2	*m*-NO_2	*p*-NO_2
C1-C2	-2.13	-1.83	-2.38	-2.05	-2.01	-2.60	-2.62
para	-2.68	-2.49	-2.92	-2.55	-2.65	-3.14	-3.24
dia	0.55	0.66	0.55	0.50	0.64	0.55	0.62
C1-C6	-2.13	-1.61	-2.22	-2.05	-1.64	-2.19	-2.62
para	-2.68	-1.57	-2.70	-2.55	-1.98	-2.73	-3.24
dia	0.55	-0.04	0.48	0.50	0.35	0.55	0.62
C2-C3	-0.33	-0.35	-0.25	-0.36	-0.22	-0.24	-0.37
para	-0.37	-0.39	-0.30	-0.35	-0.30	-0.28	-0.37
dia	0.04	0.04	0.05	0.01	0.08	0.04	0.00
C5-C6	-0.33	-0.26	-0.31	-0.36	-0.29	-0.33	-0.37
para	-0.37	-0.38	-0.18	-0.35	-0.35	-0.30	-0.37
dia	0.04	0.12	-0.13	0.01	0.06	-0.03	0.00
C3-C4	-0.04	-0.01	-0.06	-0.05	0.05	-0.07	-0.11
para	-0.60	-0.56	-0.59	-0.60	-0.49	-0.60	-0.69
dia	0.56	0.55	0.53	0.55	0.54	0.53	0.58
C4-C5	-0.04	0.01	-0.06	-0.05	-0.02	-0.11	-0.11
para	-0.60	-0.54	-0.71	-0.60	-0.55	-0.72	-0.69
dia	0.56	0.55	0.65	0.55	0.53	0.61	0.58

C-C$_{total}$	**-5.00**	**-4.05**	**-5.28**	**-4.92**	**-4.13**	**-5.54**	**-6.18**
para	**-7.30**	**-5.92**	**-7.40**	**-7.01**	**-6.31**	**-7.77**	**-8.57**
dia	**2.30**	**1.88**	**2.12**	**2.09**	**2.19**	**2.23**	**2.40**
C1-H	27.10	26.84	27.17	27.08	26.14	26.97	27.14
para	2.66	2.28	2.63	2.50	2.57	2.83	2.97
dia	24.44	24.56	24.54	24.58	23.57	24.14	24.17
C2-H	-0.27	-0.30	-0.21	-0.24	-0.33	-0.26	-0.18
para	-1.12	-1.16	-1.01	-1.09	-1.21	-1.14	-1.06
dia	0.85	0.86	0.81	0.85	0.88	0.88	0.88
C6-H	-0.27	/	-0.23	-0.24	/	-0.21	-0.18
para	-1.12	/	-1.10	-1.09	/	-1.14	-1.06
dia	0.85	/	0.87	0.85	/	0.93	0.88
C3-H	-0.06	-0.06	-0.08	-0.07	-0.08	-0.06	-0.03
para	-0.24	-0.24	-0.24	-0.19	-0.27	-0.25	-0.23
dia	0.18	0.18	0.16	0.12	0.19	0.19	0.20
C5-H	-0.06	-0.04	/	-0.07	-0.05	/	-0.03
para	-0.24	-0.27	/	-0.19	-0.28	/	-0.23
dia	0.18	0.23	/	0.12	0.23	/	0.20
C4-H	-0.09	-0.08	-0.07	/	-0.09	-0.05	/
para	-0.08	-0.06	-0.07	/	-0.08	-0.07	/
dia	-0.01	-0.02	0.00	/	-0.01	0.02	/
C-H$_{total}$	**26.35**	**26.36**	**26.58**	**26.46**	**25.59**	**26.39**	**26.72**
para	**-0.13**	**0.56**	**0.22**	**-0.07**	**0.73**	**0.24**	**0.38**
dia	**26.46**	**25.80**	**26.36**	**26.53**	**24.86**	**26.15**	**26.34**
C=C$_{total}$	**2.27**	**2.35**	**2.66**	**2.89**	**2.05**	**2.40**	**2.28**
para	**-3.57**	**-3.32**	**-3.10**	**-3.06**	**-3.60**	**-3.36**	**-3.33**
dia	**5.83**	**5.67**	**5.76**	**5.95**	**5.65**	**5.76**	**5.61**
CR (C)$_{total}$	**0.47**	**0.40**	**0.60**	**0.61**	**0.26**	**0.72**	**0.98**
para	**0.89**	**0.83**	**1.03**	**1.08**	**0.67**	**1.13**	**1.39**
dia	**-0.42**	**-0.43**	**-0.43**	**-0.47**	**-0.41**	**-0.41**	**-0.41**
C-N	/	-0.50	-0.19	-0.17	-0.26	-0.02	-0.01
para	/	-1.59	-0.27	0.01	1.02	0.13	0.38
dia	/	1.09	-0.08	-0.18	-0.76	-0.15	-0.39
N-H$_{total}$	/	0.06	0.08	0.06	/	/	/
para	/	-0.80	-0.66	-0.66	/	/	/
dia	/	0.86	0.74	0.72	/	/	/
N-O$_{total}$	/	/	/	/	0.53	0.23	0.18
para	/	/	/	/	-0.70	-0.83	-0.90
dia	/	/	/	/	1.24	1.06	1.08
N=O	/	/	/	/	1.04	0.27	0.16
para	/	/	/	/	-0.69	-0.53	-0.27
dia	/	/	/	/	1.74	0.80	0.43
LP$_{\pi}$	/	0.41	0.00	0.05	-0.52	-0.19	-0.12
para	/	-0.06	-0.05	-0.09	-0.06	0.05	-0.18

dia	/	0.47	0.05	0.14	-0.46	-0.24	0.06
LP_{other}	/	/	/	/	-1.23	-0.30	-0.26
para	/	/	/	/	0.77	0.43	0.33
dia	/	/	/	/	-2.00	-0.73	-0.59
CR $(N/O)_{total}$	/	-0.04	-0.02	-0.02	-0.06	-0.02	-0.02
para	/	-0.01	0.00	0.00	-0.04	0.00	0.00
dia	/	-0.03	-0.02	-0.02	-0.02	-0.02	-0.02
R	**/**	**-0.48**	**-0.13**	**-0.13**	**-1.02**	**-0.11**	**-0.09**
para	**/**	**-2.39**	**-0.94**	**-0.64**	**-1.00**	**-0.26**	**-0.19**
dia	**/**	**1.92**	**0.81**	**0.51**	**-0.02**	**0.15**	**0.10**
π_{total}	**2.27**	**2.76**	**2.65**	**2.94**	**2.57**	**2.48**	**2.32**
para	**-3.57**	**-3.40**	**-3.15**	**-3.12**	**-4.34**	**-3.85**	**-3.78**
dia	**5.83**	**6.16**	**5.80**	**6.06**	**6.91**	**6.33**	**6.10**
Total	**24.09**	**24.99**	**24.42**	**24.96**	**23.27**	**23.94**	**23.75**
para	**-10.11**	**-10.34**	**-10.24**	**-9.73**	**-10.25**	**-10.52**	**-10.76**
dia	**34.19**	**35.34**	**34.67**	**34.69**	**33.52**	**34.46**	**34.51**

References

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2. Yang, H.; Li, Y.; Jiang, M.; Wang J.; Fu, H. *Chem. Eur. J.* **2011**, *17*, 5652-5660.

Absolute energies and x, y, z coordinates of the optimized structures at the BPW91/6-311++G(d,p) level

Benzene

E = -232.2749331 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	1.401775	0.000000
2	6	0	1.213973	0.700887	0.000000
3	6	0	1.213973	-0.700888	0.000000
4	6	0	0.000000	-1.401775	0.000000
5	6	0	-1.213973	-0.700887	0.000000
6	6	0	-1.213973	0.700888	0.000000
7	1	0	0.000000	2.493267	0.000000
8	1	0	2.159233	1.246633	0.000000
9	1	0	2.159233	-1.246634	0.000000
10	1	0	0.000000	-2.493267	0.000000
11	1	0	-2.159233	-1.246634	0.000000
12	1	0	-2.159233	1.246634	0.000000

Aniline

E = -287.650898 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.001820	-1.175802	1.206893
2	6	0	0.001820	0.222024	1.213193
3	6	0	0.002002	0.944978	0.000000
4	6	0	0.001820	0.222024	-1.213193
5	6	0	0.001820	-1.175802	-1.206893
6	6	0	0.002552	-1.889371	0.000000
7	1	0	-0.000432	-1.711741	2.158175
8	1	0	0.003405	0.764048	2.161769
9	1	0	0.003405	0.764048	-2.161769
10	1	0	-0.000432	-1.711741	-2.158175
11	1	0	0.001644	-2.979892	0.000000
12	7	0	0.067404	2.341926	0.000000
13	1	0	-0.275214	2.796745	-0.841832
14	1	0	-0.275214	2.796745	0.841832

Nitrobenzene

E = -436.8488854 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	0.000000	1.225665	-0.432694
2	6	0	0.000000	1.216402	-1.829760
3	6	0	0.000000	0.000000	-2.527125
4	6	0	0.000000	-1.216402	-1.829760
5	6	0	0.000000	-1.225665	-0.432694
6	6	0	0.000000	0.000000	0.242292
7	1	0	0.000000	2.155588	0.132466
8	1	0	0.000000	2.160958	-2.374124
9	1	0	0.000000	0.000000	-3.617814
10	1	0	0.000000	-2.160958	-2.374124
11	1	0	0.000000	-2.155588	0.132466
12	7	0	0.000000	0.000000	1.724290
13	8	0	0.000000	1.094347	2.305596
14	8	0	0.000000	-1.094347	2.305596