Supplementary Information for 'The unexpected roles of σ and π orbitals in electron donor and acceptor group effects on the ^{13}C NMR chemical shifts in substituted benzenes'

1 Experimental ^{13}C NMR chemical shifts

Table S1: Experimental carbon 1 ^{13}C NMR chemical shifts[a,b] for R group in *ortho* (*o*-), *meta* (*m*-), and *para* (*p*-) position related to C1 of R-benzene compounds in $CDCl_3$ and DMSO-d_6.

				R			
Solvent	H	*o*-NH_2	*m*-NH_2	*p*-NH_2	*o*-NO_2	*m*-NO_2	*p*-NO_2
$CDCl_3$	128.55	115.29	129.45	118.73	123.65	129.48	134.76
DMSO-d_6	128.25	113.84	128.76	115.61	123.22	129.77	135.19

[a] in ppm. [b] Experimental error is 0.1 ppm.

2 Individual contributions of the C1 shielding

Table S2 displays the decomposition of the C1 isotropic NMR shielding constants into the diamagnetic and paramagnetic contributions.

Table S2: The C1 shielding (σ_{total}[a,b]) and the diamagnetic (σ_{dia}[a]) and paramagnetic (σ_{para}[a]) contributions obtained for R-benzene compounds.

				R			
	H	*o*-NH_2	*m*-NH_2	*p*-NH_2	*o*-NO_2	*m*-NO_2	*p*-NO_2
σ_{dia}	241.87	242.72	241.04	242.10	241.44	241.50	241.66
σ_{para}	-187.99	-173.47	-188.27	-175.65	-184.24	-187.96	-195.96
σ_{total}	53.88	69.25	52.77	66.45	57.20	53.54	45.70

[a] in ppm. [b] $\sigma_{total} = \sigma_{dia} + \sigma_{para}$.

3 NLMO contributions to the C1 shielding

NLMO contributions for diamagnetic and paramagnetic terms of the C1 shielding are displayed in Table S3 and S4, respectively, for R-benzenes.

Table S3: NLMO contributions[a] to σ_{dia} term of the C1 shielding for R-benzenes.

Parent				R			
NBO	H	*o*-NH_2	*m*-NH_2	*p*-NH_2	*o*-NO_2	*m*-NO_2	*p*-NO_2
CR (C1)	203.54	203.50	203.54	203.50	203.55	203.54	203.55
CR (C2-C6)[b]	0.03	0.04	0.04	0.04	0.03	0.03	0.03
CR (N)	-	0.00	0.00	0.00	0.00	0.00	0.00
CR (O)[c]	-	-	-	-	0.00	0.00	0.00
LP (N)	-	0.57	0.09	0.24	-	-	-
LP_1(O)[c]	-	-	-	-	0.73	0.41	0.32
LP_2(O)[c]	-	-	-	-	-0.40	-0.15	-0.14
LP_3(O)	-	-	-	-	0.07	0.01	0.02
$\sigma_{C1\text{-}C2}$	7.79	6.77	7.23	7.60	5.56	7.30	7.91
$\sigma_{C1\text{-}C6}$	7.79	8.47	7.86	7.60	8.46	7.66	7.91
$\sigma_{C2\text{-}C3}$	0.39	0.50	0.41	0.33	0.66	0.25	0.32
$\sigma_{C3\text{-}C4}$	-0.12	-0.12	-0.04	-0.04	-0.12	-0.01	-0.09
$\sigma_{C4\text{-}C5}$	-0.12	-0.12	-0.14	-0.04	-0.13	-0.14	-0.09
$\sigma_{C5\text{-}C6}$	0.39	0.45	0.35	0.33	0.41	0.37	0.32
$\pi_{C\text{-}C}$[d]	18.87	19.47	18.77	19.36	18.42	18.86	18.29
$\sigma_{C1\text{-}H}$	2.30	2.81	2.16	2.32	3.23	2.39	2.26
$\sigma_{C2\text{-}H}$	0.40	-	0.46	0.39	-	0.46	0.41
$\sigma_{C2\text{-}R}$	-	-0.02	-	-	0.32	-	-
$\sigma_{C3\text{-}H}$	0.08	0.08	-	0.12	0.07	-	0.12
$\sigma_{C3\text{-}R}$	-	-	-0.06	-	-	0.07	-
$\sigma_{C4\text{-}H}$	0.05	0.05	0.07	-	0.05	0.08	-
$\sigma_{C4\text{-}R}$	-	-	-	-0.04	-	-	0.05
$\sigma_{C5\text{-}H}$	0.08	0.08	0.06	0.12	0.06	0.06	0.12
$\sigma_{C6\text{-}H}$	0.40	0.37	0.41	0.39	0.40	0.38	0.41
$\sigma_{N\text{-}H}$[e]	-	-0.18	-0.17	-0.12	-	-	-
$\sigma_{N\text{-}O}$[f]	-	-	-	-	-0.22	-0.11	-0.10
$\pi_{N\text{-}O}$	-	-	-	-	0.29	0.04	0.04
$\sum_{total}$[g]	241.87	242.72	241.04	242.10	241.44	241.50	241.66

[a] in ppm. [b] Sum of core carbon 2-6 contributions. [c] Sum of contributions from two oxigen atoms. [d] Sum of three π orbitals. [e] Sum of $\sigma_{N\text{-}H}$ contributions. [f] Sum of $\sigma_{N\text{-}O}$ contributions. [g] Sum of all NLMO contributions.

Table S4: NLMO contributions[a] to σ_{para} term of the C1 shielding for R-benzenes.

Parent NBO	H	*o*-NH_2	*m*-NH_2	*p*-NH_2	*o*-NO_2	*m*-NO_2	*p*-NO_2
				R			
CR (C1)	0.01	0.02	0.01	0.01	0.02	0.01	0.01
CR (C2-C6)[b]	-0.94	-0.94	-0.94	-0.85	-1.05	-0.91	-0.82
CR (N)	-	-0.01	0.00	0.00	-0.01	-0.01	0.00
CR (O)[c]	-	-	-	-	-0.04	-0.03	-0.02
LP (N)	-	-0.06	-0.63	-0.01	-	-	-
LP_1(O)[c]	-	-	-	-	-1.04	-0.35	-0.42
LP_2(O)[c]	-	-	-	-	-2.40	-0.30	-0.16
LP_3(O)	-	-	-	-	-0.68	-0.30	-0.22
$\sigma_{C1\text{-}C2}$	-56.14	-52.61	-58.36	-50.95	-60.91	-59.07	-54.35
$\sigma_{C1\text{-}C6}$	-56.14	-51.60	-54.71	-50.95	-51.11	-49.31	-54.35
$\sigma_{C2\text{-}C3}$	-2.26	-2.70	-2.05	-2.39	-2.99	-2.43	-2.66
$\sigma_{C3\text{-}C4}$	-0.15	-0.08	-0.32	-0.29	0.05	-0.33	-0.27
$\sigma_{C4\text{-}C5}$	-0.15	0.00	-0.37	-0.29	0.06	-0.42	-0.27
$\sigma_{C5\text{-}C6}$	-2.26	-2.02	-2.08	-2.39	-1.65	-2.16	-2.66
$\pi_{C\text{-}C}$[d]	-3.44	-2.42	-2.11	-1.88	-2.13	-3.19	-4.21
$\sigma_{C1\text{-}H}$	-58.62	-52.67	-59.10	-58.16	-55.47	-62.75	-69.69
$\sigma_{C2\text{-}H}$	-3.30	-	-3.34	-3.22	-	-2.99	-3.07
$\sigma_{C2\text{-}R}$	-	-2.47	-	-	-1.35	-	-
$\sigma_{C3\text{-}H}$	-0.48	-0.26	-	-0.42	-0.71	-	-0.08
$\sigma_{C3\text{-}R}$	-	-	-0.32	-	-	0.00	-
$\sigma_{C4\text{-}H}$	-0.34	-0.36	-0.33	-	-0.39	-0.34	-
$\sigma_{C4\text{-}R}$	-	-	-	-0.28	-	-	0.03
$\sigma_{C5\text{-}H}$	-0.48	-0.73	-0.43	-0.42	-0.59	-0.30	-0.08
$\sigma_{C6\text{-}H}$	-3.30	-2.94	-3.17	-3.22	-2.79	-3.25	-3.05
$\sigma_{N\text{-}H}$[e]	-	-1.62	-0.02	0.06	-	-	-
$\sigma_{N\text{-}O}$[f]	-	-	-	-	0.27	0.21	0.16
$\pi_{N\text{-}O}$	-	-	-	-	0.67	0.26	0.22
$\sum_{total}$[g]	-187.99	-173.47	-188.27	-175.65	-184.24	-187.96	-195.96

[a] in ppm. [b] Sum of core carbon 2-6 contributions. [c] Sum of contributions from two oxigen atoms. [d] Sum of three π orbitals. [e] Sum of $\sigma_{N\text{-}H}$ contributions. [f] Sum of $\sigma_{N\text{-}O}$ contributions. [g] Sum of all NLMO contributions.

Table S5: Atomic hybrid contributions (%) of C1 and C2 to the $\sigma_{C1\text{-}C2}$ NLMO for R-benzene.

	R						
	H	*o*-NH_2	*m*-NH_2	*p*-NH_2	*o*-NO_2	*m*-NO_2	*p*-NO_2
%C1	49.67	48.89	49.17	49.50	48.57	48.93	49.56
%C2	49.67	50.24	50.04	49.81	50.62	50.14	49.79

Table S6: Atomic hybrid contributions (%) of C1 and C6 to the $\sigma_{C1\text{-}C6}$ NLMO for R-benzene.

	R						
	H	*o*-NH_2	*m*-NH_2	*p*-NH_2	*o*-NO_2	*m*-NO_2	*p*-NO_2
%C1	49.67	50.05	49.81	49.50	50.15	49.79	49.56
%C6	49.67	49.16	49.49	49.81	48.92	49.56	49.79

Table S7: Atomic hybrid contributions (%) of C1 and H to the $\sigma_{C1\text{-}H}$ NLMO for R-benzene.

	R						
	H	*o*-NH_2	*m*-NH_2	*p*-NH_2	*o*-NO_2	*m*-NO_2	*p*-NO_2
%C1	61.07	60.88	60.98	60.99	62.32	61.59	61.46
%H	37.95	38.14	38.01	38.02	36.56	37.40	37.55