Classical and reverse substituent effects in *meta*- and *para*- substituted nitrobenzene derivatives

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Supplementary Information

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Table S1. SESE values for *para*- and *meta*- substituted nitrobenzene derivatives obtained at different computational levels.

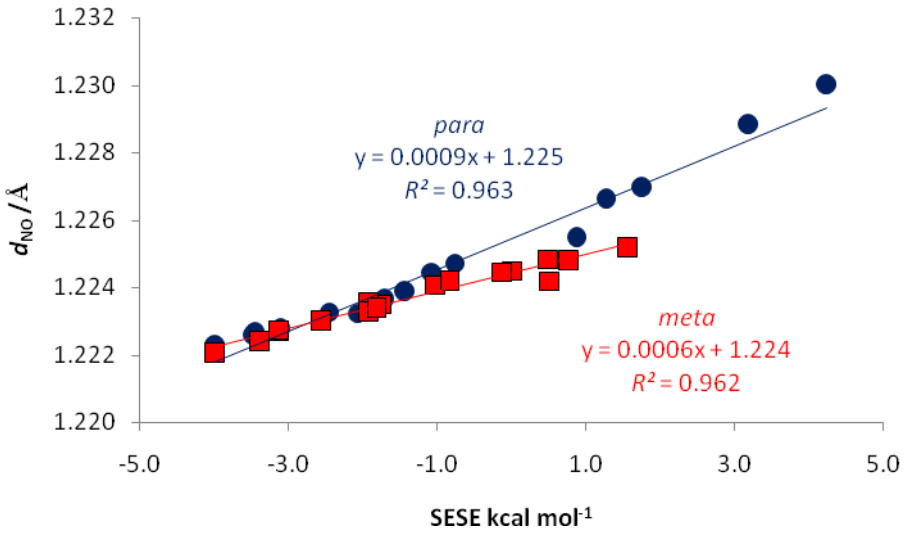
X	MP2			B3LYP			M06-2X			HF		
	6-31+G**	**6-311++G****	**aug-cc-pVDZ**	**6-31+G****	**6-311++G****	**aug-cc-pVDZ**	**6-31+G****	**6-311++G****	**aug-cc-pVDZ**	**6-31+G****	**6-311++G****	**aug-cc-pVDZ**
1	2	3	4	5	6	7	8	9	10	11	12	13
Para												
NO	-2.41	-2.07	-1.99	-3.62	-3.46	-3.32	-3.87	-3.6	-3.55	-3.45	-3.38	-3.21
NO_2	-2.77	-2.49	-2.16	-4.17	-4.01	-3.81	-4.33	-4.06	-3.95	-4.84	-4.79	-4.49
COCl	-2.14	-2.14	-1.98	-3.6	-3.49	-3.36	-3.83	-3.61	-3.6	-3.87	-3.88	-3.73
CN	-2.39	-2.25	-2.02	-3.17	-3.12	-3.01	-3.32	-3.21	-3.19	-3.78	-3.77	-3.65
CF_3	-2.24	-1.98	-1.75	-2.65	-2.58	-2.43	-2.69	-2.61	-2.50	-2.80	-2.83	-2.64
COMe	-1.11	-0.94	-0.85	-1.85	-1.72	-1.67	-1.92	-1.80	-1.79	-2.01	-1.97	-1.93
COOH	-1.27	-1.32	-0.99	-2.20	-2.08	-2.02	-2.30	-2.13	-2.14	-2.55	-2.51	-2.45
CHO	-1.66	-1.45	-1.38	-2.58	-2.46	-2.39	-2.61	-2.67	-2.66	-2.70	-2.67	-2.61
$CONH_2$	-1.05	-1.01	-0.73	-1.54	-1.45	-1.4	-1.66	-1.56	-1.57	-1.90	-1.88	-1.84
Cl	-1.00	-1.01	-0.95	-1.12	-1.09	-1.05	-1.12	-1.08	-1.12	-1.45	-1.42	-1.35
F	-1.31	-1.14	-0.89	-0.79	-0.77	-0.64	-0.72	-0.65	-0.61	-0.68	-0.67	-0.52
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Me	0.35	0.21	0.45	0.88	0.87	0.87	0.89	0.71	0.81	1.04	0.99	1.01
OMe	0.62	0.56	0.80	1.78	1.74	1.77	1.63	1.49	1.57	3.36	1.87	1.91
OH	0.14	0.12	0.37	1.34	1.27	1.34	1.40	1.26	1.34	1.50	1.41	1.51
NH_2	1.29	1.01	1.38	3.33	3.17	3.17	3.37	3.06	3.10	3.12	2.94	2.93
NMe_2	1.95	1.60	1.68	4.34	4.23	4.23	4.16	3.81	3.96	4.50	3.72	3.46
meta												
NO	-2.91	-2.55	-2.63	-3.23	-3.14	-3.00	-3.33	-3.17	-3.08	-2.63	-2.63	-2.47
NO_2	-3.79	-3.42	-3.43	-4.09	-4.00	-3.84	-4.13	-3.89	-3.84	-4.13	-4.19	-3.91
COCl	-2.73	-2.52	-2.80	-3.21	-3.14	-3.05	-3.21	-3.09	-3.08	-2.77	-2.82	-2.69
CN	-3.30	-3.09	-3.05	-3.44	-3.39	-3.33	-3.56	-3.42	-3.45	-3.56	-3.56	-3.47
CF_3	-2.68	-2.40	-2.22	-2.61	-2.57	-2.52	-2.83	-2.71	-2.64	-2.44	-2.56	-2.45
COMe	-1.78	-1.50	-1.67	-1.13	-1.04	-1.02	-1.15	-1.08	-1.07	-0.78	-0.79	-0.74
COOH	-1.91	-1.69	-1.79	-1.86	-1.75	-1.75	-1.85	-1.70	-1.76	-1.49	-1.50	-1.48
CHO	-2.33	-2.04	-2.23	-2.01	-1.93	-1.89	-1.94	-2.07	-2.05	-1.59	-1.61	-1.55
$CONH_2$	-1.83	-1.59	-1.63	-0.9	-0.84	-0.83	-0.93	-0.87	-0.92	-0.91	-0.92	-0.91
Cl	-1.46	-1.43	-1.51	-1.95	-1.93	-1.93	-2.05	-1.96	-2.10	-2.29	-2.29	-2.26
F	-1.59	-1.36	-1.26	-1.86	-1.82	-1.73	-1.94	-1.77	-1.81	-2.36	-2.30	-2.17
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Me	0.62	0.58	0.67	0.47	0.48	0.39	0.36	0.28	0.30	0.35	0.38	0.27

1	2	3	4	5	6	7	8	9	10	11	12	13
OMe	0.96	1.01	1.11	0.46	0.50	0.42	0.30	0.27	0.23	1.25	-0.11	-0.14
OH	-0.19	-0.04	-0.01	-0.12	-0.14	-0.19	-0.24	-0.27	-0.35	-0.82	-0.80	-0.79
NH_2	1.21	1.14	1.24	0.79	0.75	0.66	0.65	0.55	0.45	-0.11	-0.08	-0.13
NMe_2	1.92	1.98	2.06	1.48	1.55	1.41	1.26	1.18	1.13	1.14	0.68	0.53

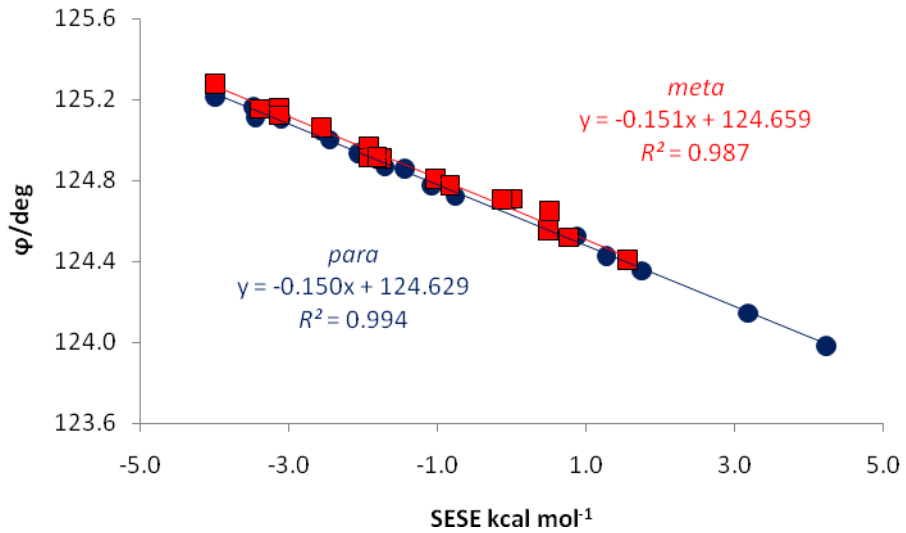
Table S2. cSAR values for *para*- and *meta*- substituted nitrobenzene derivatives based on different assessments of atomic charges.

	NBO	**Hirshfeld**	**AIM**	**NBO**	**Hirshfeld**	**AIM**
X	cSAR(X)	cSAR(X)	cSAR(X)	cSAR(NO_2)	cSAR(NO_2)	cSAR(NO_2)
para						
NO	-0.131	-0.082	-0.162	-0.147	-0.098	-0.282
NO_2	-0.170	-0.095	-0.274	-0.170	-0.095	-0.274
COCl	-0.175	-0.078	-0.166	-0.156	-0.098	-0.281
CN	-0.152	-0.095	-0.163	-0.164	-0.105	-0.282
CF_3	-0.112	-0.049	-0.143	-0.169	-0.110	-0.288
COMe	-0.090	-0.018	-0.053	-0.180	-0.119	-0.301
COOH	-0.128	-0.041	-0.122	-0.174	-0.114	-0.297
CHO	-0.114	-0.052	-0.078	-0.162	-0.110	-0.293
$CONH_2$	-0.066	-0.006	-0.051	-0.189	-0.124	-0.303
Cl	0.016	-0.003	-0.130	-0.205	-0.137	-0.304
F	0.100	0.010	-0.135	-0.216	-0.144	-0.307
H	0.042	0.033	0.031	-0,201	-0.140	-0.318
Me	0.060	0.074	0.080	-0.221	-0.155	-0.328
OMe	0.168	0.115	0.024	-0.264	-0.178	-0.338
OH	0.162	0.094	0.004	-0.252	-0.172	-0.329
NH_2	0.186	0.164	0.104	-0.286	-0.202	-0.355
NMe_2	0.219	0.211	0.157	-0.303	-0.217	-0.370
Meta						
NO	-0.152	-0.092	-0.156	-0.185	-0.114	-0.277
NO_2	-0.168	-0.102	-0.264	-0.168	-0.102	-0.264
COCl	-0.193	-0.084	-0.157	-0.181	-0.111	-0.278
CN	-0.171	-0.104	-0.157	-0.173	-0.107	-0.276
CF_3	-0.129	-0.057	-0.135	-0.183	-0.113	-0.281
COMe	-0.113	-0.025	-0.045	-0.185	-0.132	-0.305
COOH	-0.149	-0.049	-0.114	-0.193	-0.125	-0.296
CHO	-0.136	-0.061	-0.071	-0.193	-0.124	-0.292
$CONH_2$	-0.087	-0.013	-0.041	-0.195	-0.133	-0.305

Cl	-0.010	-0.016	-0.125	-0.173	-0.121	-0.289
F	0.075	-0.002	-0.128	-0.173	-0.121	-0.287
H	0.019	0.025	0.040	-0,201	-0.140	-0.318
Me	0.031	0.063	0.088	-0.198	-0.145	-0.324
OMe	0.126	0.093	0.020	-0.188	-0.137	-0.309
OH	0.129	0.076	0.005	-0.181	-0.137	-0.306
NH_2	0.163	0.130	0.092	-0.184	-0.146	-0.319
NMe_2	0.163	0.171	0.137	-0.193	-0.153	-0.329

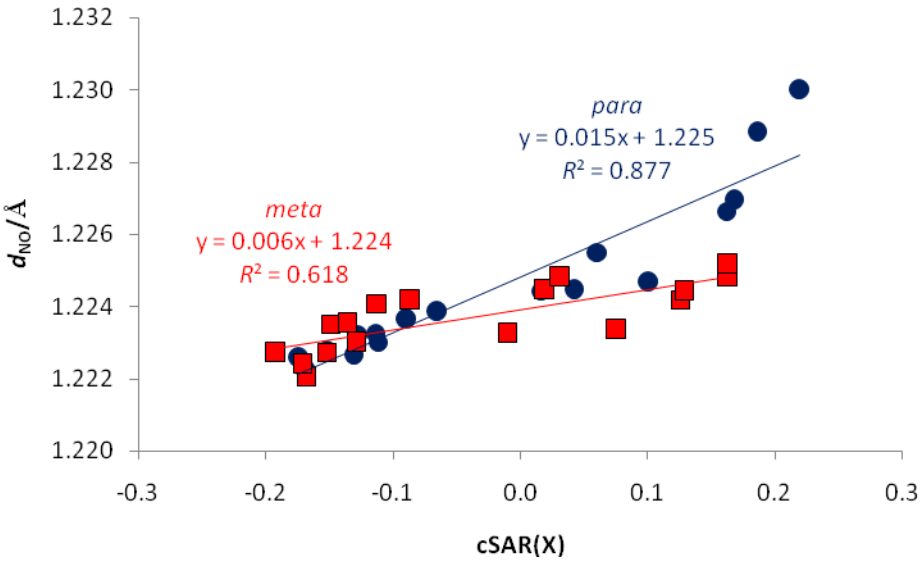


a)

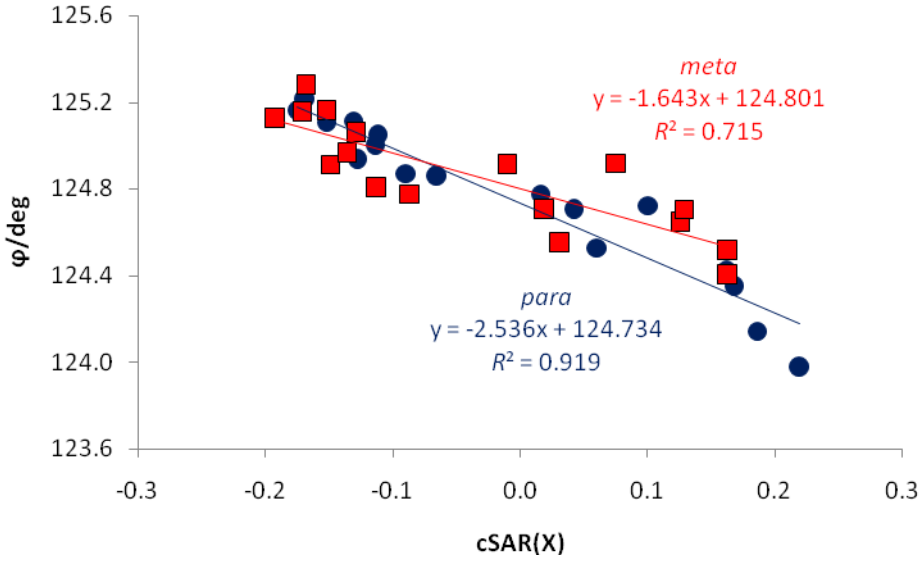


b)

Fig. S1. Dependence of d_{NO} (a) and ONO angle, φ, (b) on SESE for *meta*- and *para*-substituted nitrobenzene derivatives.



a)



b)

Fig. S2. Dependence of d_{NO} (a) and ONO angle, φ, (b) on cSAR(X) for *meta*- and *para*-substituted nitrobenzene derivatives.

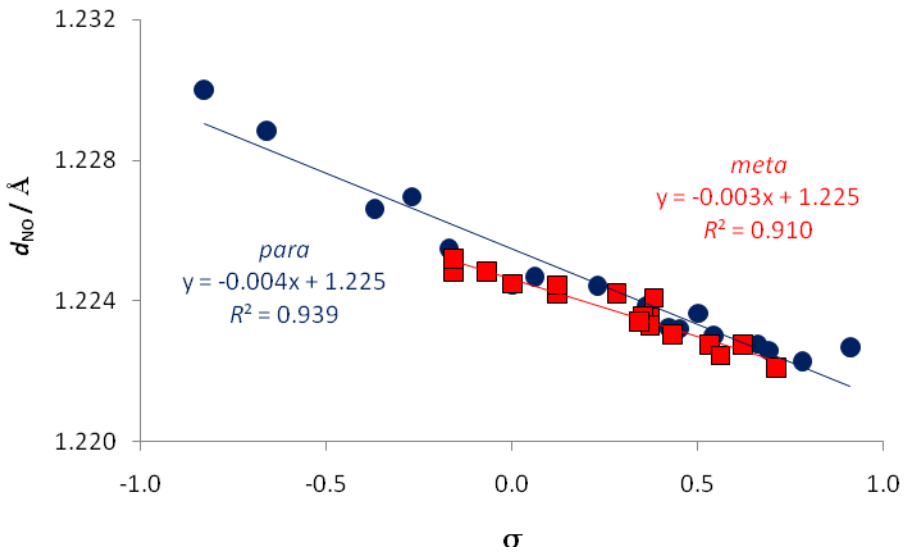


Fig. S3. Dependence of d_{NO} on σ for *meta*- and *para*- substituted nitrobenzene derivatives, for a joint set of data: y = -0.004 · x + 1.225 with R^2 = 0.903.

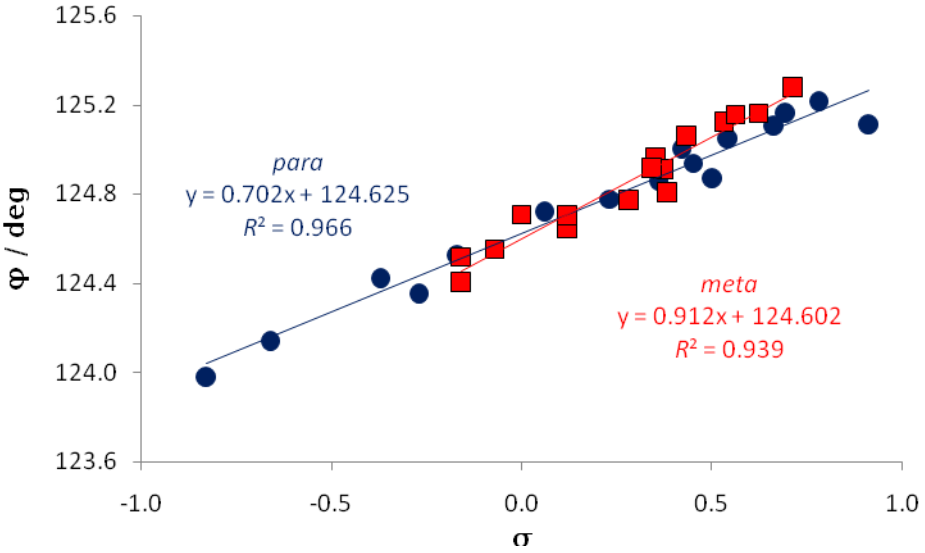


Fig. S4. Dependence of ONO angle, φ, on substituent constants, σ, for *meta*- and *para*-substituted nitrobenzene derivatives, for a joint set of data: y = 0.751 · x + 124.631 with R^2 = 0.943.

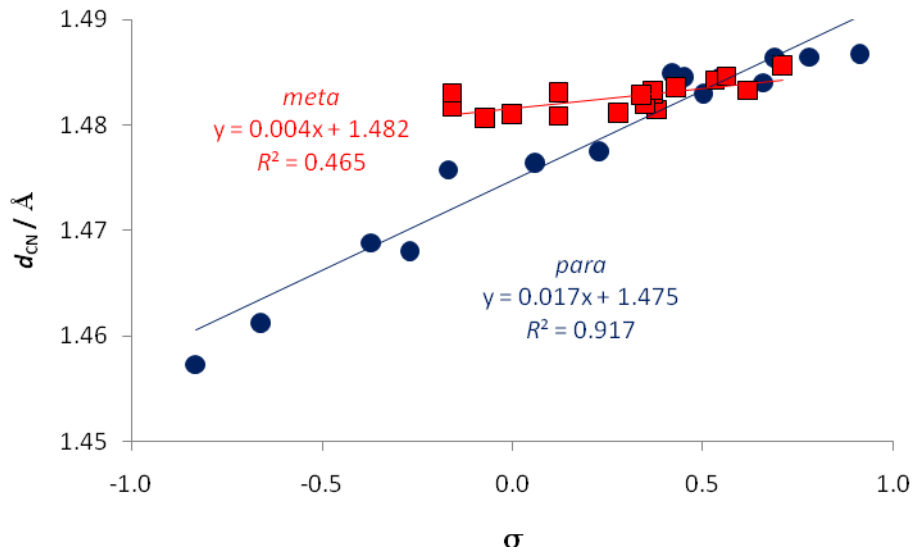


Fig. S5. The Hammett plots for d_{CN} for *meta*- and *para*- substituted nitrobenzene derivatives, for a joint set of data: y = 0.015 · x + 1.477 with R^2 = 0.765.

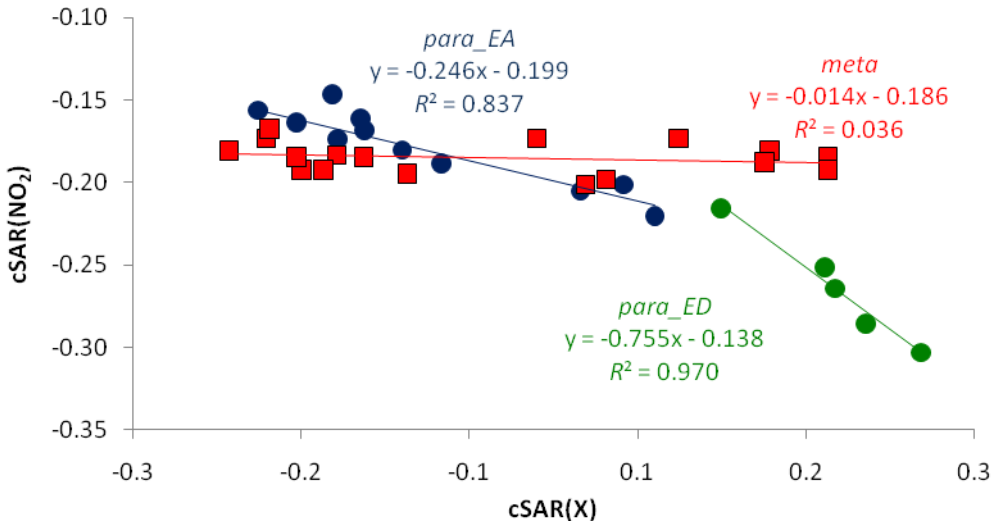


Fig. S6. Dependences of cSAR(NO_2) on cSAR(X) for *meta*- derivatives and for two set of data of *para*- ones for cSAR(X): EA and strongly ED substituents [with cSAR(X) > 0.1].

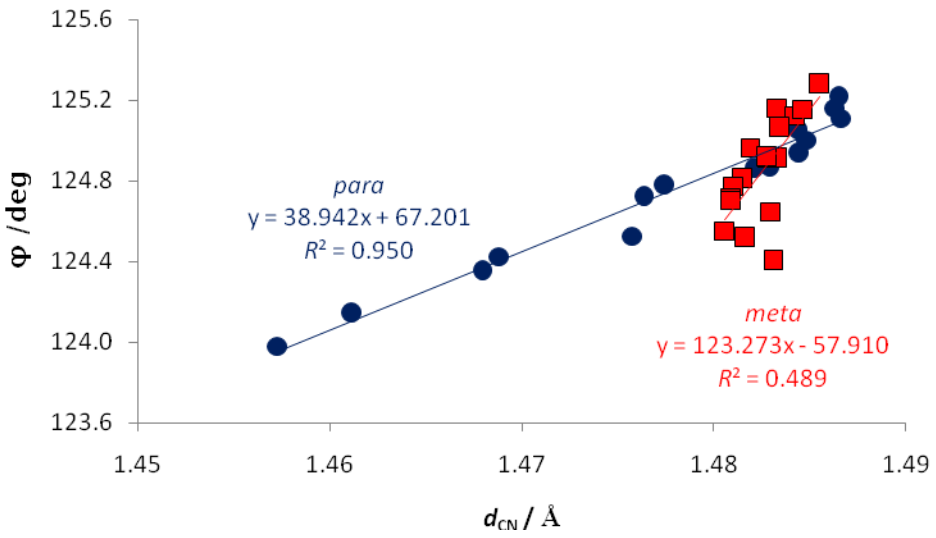


Fig. S7. Dependence of ONO angle, φ, on CN bond length, d_{CN}, for *meta*- and *para*-substituted nitrobenzene derivatives, for a joint set of data: y = 38.746 · x + 67.452 with R^2 = 0.719.

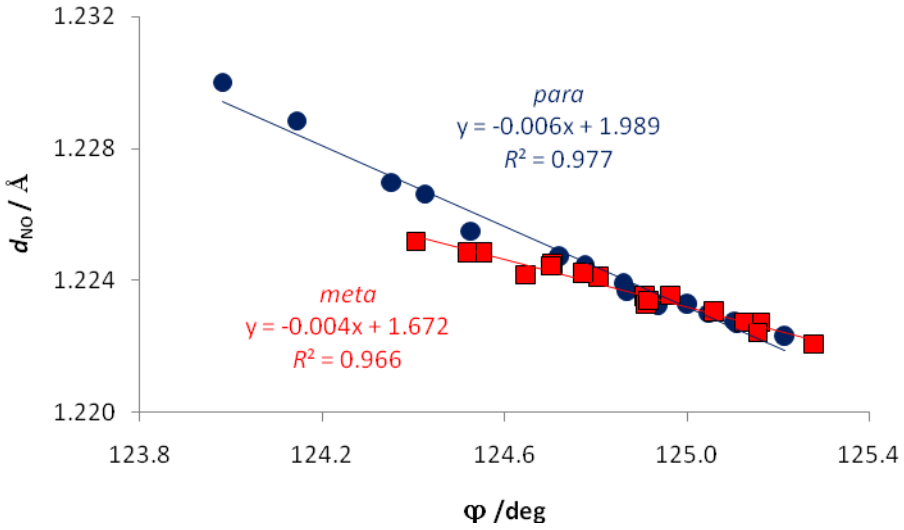


Fig. S8. Dependence of NO bond length, d_{NO}, *vs*. ONO angle, φ, for *meta*- and *para*-substituted nitrobenzene derivatives, for a joint set of data: y = -0.005 · x + 1.901 with R^2 = 0.920.