Electronic Supplementary Material (ESI) for Chemical Science.

Examining the Chemical and Structural Properties that Influence the Sensitivity of Energetic Nitrate Esters: Supplementary Material

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The parameterization of the DFTB-*lanl22* model is provided in Tables 1-4. The analytic forms for the radial dependences of the bond integrals, overlap integrals, and pair potentials are identical to those presented in A. Krishnapriyan, P. Yang, A. M. N. Niklasson, and M. J. Cawkwell, *J. Chem. Theory Comput.*, **13**, 6191 (2017).

A polynomial function, $t(R) = C_0 + (R - R_1)(C_1 + (R - R_1)(C_2 + (R - R_1)(C_3 + (R - R_1)(C_4 + (R - R_1)C_5))))$, was applied each of the bond and overlap integrals at $R_1 = 3.5$ Å to smoothly cut-off the integrals at $R_{\text{cut}} = 4.5$ Å.

Table 1: Parameterization of the Slater-Koster bond integrals, $h_{ll'\tau}(R) = h_{ll'\tau}(R_0)\exp(A_1(R-R_0)+A_2(R-R_0)^2)$.

		$ll'\tau$	$h_{ll'\tau}(R_0)$ (eV)	A_1 (Å^{-1})	A_2 (Å^{-2})	R_0 (Å)
N	O	$ss\sigma$	-9.168541	-1.451712	-0.373665	1.2
N	O	$sp\sigma$	10.517988	-0.871156	-1.546893	1.2
O	N	$sp\sigma$	10.694946	-0.641283	-0.942465	1.2
N	O	$pp\sigma$	9.101995	-0.751003	-0.642720	1.2
N	O	$pp\pi$	-5.175948	-2.019017	-0.312472	1.2
C	N	$ss\sigma$	-7.718365	-1.755704	-0.196966	1.5
C	N	$sp\sigma$	7.525992	-1.185711	-0.418180	1.5
N	C	$sp\sigma$	8.220939	-1.302831	-0.120244	1.5
C	N	$pp\sigma$	7.193983	-1.123545	-0.840286	1.5
C	N	$pp\pi$	-3.167480	-2.104650	-0.436176	1.5
C	O	$ss\sigma$	-12.082106	-2.225364	-0.739872	1.2
C	O	$sp\sigma$	9.882969	-1.181507	-0.254406	1.2
O	C	$sp\sigma$	13.269811	-1.534650	-0.106295	1.2
C	O	$pp\sigma$	8.970466	-0.652915	-1.029966	1.2
C	O	$pp\pi$	-5.335158	-2.168181	-0.229209	1.2
N	N	$ss\sigma$	-5.197621	-2.372507	-0.268676	1.5
N	N	$sp\sigma$	8.063658	-1.434943	-0.390793	1.5
N	N	$pp\sigma$	7.304169	-1.339206	-0.525704	1.5
N	N	$pp\pi$	-2.929661	-2.417591	-0.599757	1.5
O	O	$ss\sigma$	-11.251586	-1.683816	-1.107966	1.2
O	O	$sp\sigma$	11.807444	-2.061597	-0.144606	1.2
O	O	$pp\sigma$	9.203280	-0.950343	-0.948536	1.2
O	O	$pp\pi$	-4.439243	-2.330787	-0.109729	1.2
H	O	$ss\sigma$	-11.181181	-1.840474	-0.398286	1. 0
H	O	$sp\sigma$	9.159065	-1.330734	-0.429092	1.0
H	N	$ss\sigma$	-11.287291	-1.466359	-0.389508	1.0
H	N	$sp\sigma$	9.581634	-1.163687	-0.385420	1. 0
C	C	$ss\sigma$	-8.790641	-1.614757	-0.480316	1.4
C	C	$sp\sigma$	8.597915	-0.994090	-0.597650	1.4
C	C	$pp\sigma$	6.898904	-0.519066	-1.034539	1.4
C	C	$pp\pi$	-3.729192	-1.888724	-0.233726	1.4
H	C	$ss\sigma$	-8.758461	-1.330003	-0.466840	1.1
H	C	$sp\sigma$	8.100038	-0.948214	-0.527426	1.1
H	H	$ss\sigma$	-9.186911	-1.232484	-0.362465	0.75

Table 2: Parameterization of the overlap integrals, $s_{ll'\tau}(R) = s_{ll'\tau}(R_0)\exp(B_1(R-R_0) + B_2(R-R_0)^2 + B_3(R-R_0)^3 + B_4(R-R_0)^4)$.

		$ll'\tau$	$s_{ll'\tau}(R_0)$ (eV)	B_1 (Å^{-1})	B_2 (Å^{-2})	B_3 (Å^{-3})	B_4 (Å^{-4})	R_0 (Å)
N	O	$ss\sigma$	0.340064	-1.703613	-0.622348	0.036738	-0.040158	1.2
N	O	$sp\sigma$	-0.370946	-1.040947	-0.931097	0.252441	-0.115450	1.2
O	N	$sp\sigma$	-0.420014	-1.107918	-0.905594	0.188424	-0.088365	1.2
N	O	$pp\sigma$	-0.314073	0.499050	-2.914288	2.067657	-0.738439	1.2
N	O	$pp\pi$	0.223937	-1.991867	-0.537630	-0.081270	-0.004130	1.2
C	N	$ss\sigma$	0.263438	-1.754525	-0.584215	-0.007801	-0.021729	1.5
C	N	$sp\sigma$	-0.326609	-1.197485	-0.807786	0.134891	-0.084373	1.5
N	C	$sp\sigma$	-0.337943	-1.335442	-0.769693	0.119373	-0.079493	1.5
C	N	$pp\sigma$	-0.350240	-0.467439	-1.849316	1.854403	-0.988471	1.5
C	N	$pp\pi$	0.158424	-2.114409	-0.582346	-0.051076	-0.006183	1.5
C	O	$ss\sigma$	0.375339	-1.547372	-0.642492	0.020614	-0.026699	1.2
C	O	$sp\sigma$	-0.373027	-0.776043	-1.019920	0.257539	-0.102838	1.2
O	C	$sp\sigma$	-0.458068	-1.035067	-0.937868	0.190562	-0.077841	1.2
C	O	$pp\sigma$	-0.322293	0.795473	-3.476601	2.589965	-0.897800	1.2
C	O	$pp\pi$	0.244570	-1.922717	-0.573671	-0.057280	-0.004108	1.2
N	N	$ss\sigma$	0.231654	-1.879002	-0.572765	-0.004579	-0.031106	1.5
N	N	$sp\sigma$	-0.305271	-1.385158	-0.751032	0.114531	-0.090839	1.5
N	N	$pp\sigma$	-0.324668	-0.547805	-1.638658	1.495168	-0.827868	1.5
N	N	$pp\pi$	0.142909	-2.162036	-0.571942	-0.071640	-0.004682	1.5
O	O	$ss\sigma$	0.296445	-1.911896	-0.663451	0.038054	-0.046608	1.2
O	O	$sp\sigma$	-0.362143	-1.285274	-0.939591	0.204641	-0.106438	1.2
O	O	$pp\sigma$	-0.312044	0.121814	-2.519352	1.681266	-0.644566	1.2
O	O	$pp\pi$	0.193010	-2.168462	-0.580629	-0.105104	0.004891	1.2
H	O	$ss\sigma$	0.404725	-1.702546	-0.707938	0.074904	-0.039922	1.0
H	O	$sp\sigma$	-0.447660	-0.952979	-1.163537	0.400616	-0.156965	1.0
H	N	$ss\sigma$	0.446693	-1.500463	-0.657448	0.065741	-0.037004	1.0
H	N	$sp\sigma$	-0.501530	-0.785734	-1.123232	0.394878	-0.148501	1.0
C	C	$ss\sigma$	0.346977	-1.519820	-0.570812	-0.013518	-0.015829	1.4
C	C	$sp\sigma$	-0.400467	-0.984048	-0.853949	0.157178	-0.073381	1.4
C	C	$pp\sigma$	-0.382417	0.102889	-2.786680	2.646356	-1.134320	1.4
C	C	$pp\pi$	0.214357	-1.948923	-0.578323	-0.034356	-0.007257	1.4
H	C	$ss\sigma$	0.416003	-1.459596	-0.654874	0.009140	-0.012658	1.1
H	C	$sp\sigma$	-0.495695	-0.901626	-1.007214	0.189808	-0.057087	1.1
H	H	$ss\sigma$	0.575007	-1.391261	-0.778831	0.080209	-0.017759	0.75

Table 3: On-site energies, ϵ_l, and Hubbard U parameters for C, H, N, and O.

	ϵ_s (eV)	ϵ_p (eV)	U (eV)
C	-13.811288	-5.623091	13.150637
H	-5.911651	-	12.472702
N	-19.015627	-9.619622	15.949008
O	-21.820289	-9.713321	14.960022

Table 4: Parameterization of the repulsive pair potentials, $\Phi(R) = \Phi_0 \exp(D_1 R + D_2 R^2 + D_3 R^3 + D_4 R^4)$. A cut-off tail, $t(R)$, is applied between $R = R_1$ and $R = R_{\text{cut}}$.

		Φ_0 (eV)	D_1 (Å^{-1})	D_2 (Å^{-2})	D_3 (Å^{-3})	D_4 (Å^{-4})	R_1 (Å)	R_{cut} (Å)
N	O	12.458845	19.932653	-46.634011	38.388044	-12.645469	1.6	1.7
C	N	94.105450	10.256216	-27.688867	22.077875	-6.774590	1.6	1.7
N	N	39.448545	15.007021	-36.615545	29.162650	-8.974964	1.6	1.7
C	O	0.912111	30.130162	-59.613482	45.114396	-13.229292	1.5	1.6
N	H	0.617018	28.083667	-63.418587	53.202917	-17.530345	1.3	1.4
O	O	13.936490	19.240523	-45.666442	38.070896	-12.351349	1.5	1.6
O	H	0.483473	33.157847	-81.140008	74.999003	-26.814588	1.2	1.3
C	H	1.106170	28.590048	-71.508031	65.971537	-23.421359	1.2	1.3
C	C	3.967366	24.432912	-51.160771	39.035097	-11.311238	1.6	1.7
H	H	7.986670	17.571219	-76.834340	103.953015	-53.639897	0.8	0.9