Supplemental Information

Polarizable Empirical Force Field for Aromatic Compounds Based on the Classical Drude Oscillator

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Table S1) Geometric data for benzene and toluene. In each row the upper values are from the polarizable model and the lower values are the target data.

	Benzene (drude)	Toluene (drude)
C(arom)-C(arom)	1.396 (1.392)[a]	1.403 (1.380)[b]
C(arom)-C(met)	-	1.498 (1.490)[b]
C(arom)-H	1.080 (1.080)[a]	1.077 (0.945)[b]
C(methyl)-H	-	1.111 (0.969)[b]
C(arom)- C(arom)- C(arom)	120.0	120.0 (120.0)
C(arom)- C(arom)- C(met)	-	120.0 (120.6)

a) From Gauss and Stanton, *J. Phys. Chem. A* **2000**, *104*, 2865.
b) Average values from CSD searches

Table S2) Vibrational spectra for benzene and toluene

Benzene											
Drude					**MP2/6-31G***					**Experimental**	
Freq.	PED	%	PED	%	Freq.	PED	%	PED	%	Freq.	Assign
417.1	asytor	92			374.8	asytor	88			410	Ring Deform
417.1	asytor'	92			374.8	asytor’	88			410	Ring Deform
626.3	puck	85	wagCH	15	477.3	puck	100			606	Ring Deform
663.1	asydef	60	sCC	20	584.8	asydef’	67	asydef	25	673	CH bend
663.1	asydef'	60	sCC	20	584.9	asydef	67	asydef’	25		
701.0	wagCH	100			647.2	wagCH	100			703	Ring Deform
854.9	wagCH	100			797	wagCH	100			849	CH bend
854.9	wagCH	100			797	wagCH	100				
928.4	tridef	100			844.5	wagCH	88			975	CH bend
929.9	sCC	100			844.5	wagCH	88			992	Ring str
948.6	sCC	80	rockCH	20	848.4	wagCH	100				
948.6	sCC	80	rockCH	20	964.9	tridef	100			995	CH bend
997.8	wagCH	92			969.1	sCC	99			1010	Ring Deform
997.8	wagCH	92			1021.9	sCC	67	rockCH	33	1038	CH bend
1012.0	wagCH	85	Puck	15	1021.9	sCC	67	rockCH	33		
1169.8	rockCH	62	sCC	31	1140.8	rockCH	92			1150	CH bend
1169.8	rockCH	62	sCC	31	1160.1	rockCH	77	sCC	23	1178	CH bend
1232.7	rockCH	80	sCC	20	1160.1	rockCH	77	sCC	23		
1389.4	rockCH	100			1312.2	rockCH	100			1310	Ring str
1451.3	sCC	80	rockCH	20	1380.7	sCC	92			1326	CH bend
1451.9	rockCH	80	sCC	20	1451.8	rockCH	67	sCC	33	1486	Ring str + deform
1451.9	rockCH	80	sCC	20	1451.8	rockCH	67	sCC	33		
1511.1	sCC	49	rockCH	38	1576.5	sCC	70	rockCH	20	1596	Ring str
1511.2	sCC	49	rockCH	38	1576.5	sCC	70	rockCH	20	1596	Ring str
3053.2	sCH	100			3033.7	sCH	100			3047	CH str
3053.2	sCH	100			3042.9	sCH	100				
3057.0	sCH	100			3042.9	sCH	100			3062	CH str
3057.0	sCH	100			3056.7	sCH	99			3063	CH str
3057.1	sCH	100			3056.7	sCH	99			3063	CH str
3057.3	sCH	100			3065.3	sCH	99			3068	CH str
Toluene											
Drude					**MP2/6-31G* (No experimental data analyzed for toluene)**						
22.8	tMethyl	100			56	tMethyl	100				
215.9	wagCH	86			195.1	wagCH	82				
347.2	rCCm	85			324.9	rCCm	84				
405.7	asytor	62	asytor'	29	375.9	asytor	59	asytor'	29		
452.1	asytor'	57	wagCH	24	425.8	asytor'	54	wagCH	27		
506.7	asydef'	45	bCMet	39	474.6	puck	98				
623.6	puck	81	wagCH	17	498.7	asydef'	76	bCMet	15		
678.3	asydef	82	sCC	17	599.9	asydef	88				

763.2	wagCH	86			682.5	wagCH	96				
766.9	asydef'	28	sCC	25	763.9	sCC	33	bCMet	31		
880.9	wagCH	100			787.9	wagCH	100				
946.5	tridef	53	sCC	37	811.1	wagCH	95				
959.5	wagCH	79			833.8	wagCH	89	asytor	16		
974.4	sCC	81			837.3	wagCH	96				
990.6	sCC	48	MeRock'	36	965.9	tridef	65	sCC	34		
1011.3	wagCH	81			970.6	MeRock'	69	sCC	25		
1030.8	wagCH	92			1009.6	sCC	71	rockCH	21		
1041.2	MeRock'	42	sCC	31	1021.6	MeRock	86				
1054	MeRock	64	wagCH	17	1073.8	sCC	44	rockCH	42		
1118.1	sCC	46	bCMet	24	1145.9	rockCH	87				
1177.7	rockCH	54	sCC	26	1165	rockCH	77	sCC	24		
1207.1	rockCH	67	sCC	29	1192.6	bCMet	42	sCC	24		
1346	rockCH	64	sCC	19	1291.2	rockCH	87				
1404.9	rockCH	35	MeASde	30	1380	sCC	87				
1424.1	MeASde'	42	MeSymDe	25	1385	MeSymDe	96				
1431.8	rockCH	58	sCC	26	1420.1	rockCH	50	sCC	38		
1444.3	sCC	51	MeASde	20	1460.8	MeASde'	70	MeASde	23		
1451.3	rockCH	34	MeSymDe	25	1470	rockCH	58	sCC	36		
1469.4	rockCH	49	sCC	27	1470.9	MeASde	63	MeASde'	21		
1484.8	sCC	45	rockCH	39	1567.6	sCC	70	rockCH	16		
1525.7	sCC	31	rockCH	27	1588.5	sCC	68	rockCH	19		
2845.4	sCHmet	100			2922.8	sCHmet	100				
2915.3	sCHmet	100			2998.3	sCHmet	100				
2915.9	sCHmet	100			3013.8	sCHmet	99				
3052.7	sCHar	100			3027	sCHar	100				
3054	sCHar	100			3028.4	sCHar	98				
3055.7	sCHar	100			3041.7	sCHar	100				
3056.6	sCHar	100			3049.4	sCHar	99				
3058	sCHar	100			3061	sCHar	99				

Experimental data from reference 86 and PED as defined in reference 64.

Table S3) Final force field parameters for the presented models of benzene and toluene

Benzene		
	Charges	Polarizabilities
C	-0.080	-1.376
H	0.080	0.000
Toluene		
	Charges	Polarizabilities
CG	0.036	-0.875
CD1	-0.088	-1.214
HD1	0.099	0.000
CD2	-0.088	-1.214
HD2	0.099	0.000
CE1	-0.119	-1.376
HE1	0.098	0.000
CE2	-0.119	-1.376
HE2	0.098	0.000
CZ	-0.125	-1.376
HZ	0.098	0.000
CT	-0.226	-1.473
H11	0.079	0.000
H12	0.079	0.000
H13	0.079	0.000
LJ parameters		
	Epsilon	Rmin/2
CA	-0.0680	2.0000
HP	-0.0430	1.3000
CT3	-0.0780	2.0400
HA3	-0.0240	1.3400
Bonds		
	K_b (kcal·mol^{-1}·Å^{-2})	b_0 (Å)
CA CA	305.000	1.3750
HP CA	340.000	1.0800
CT3 CA	230.000	1.4900
CT3 HA3	322.000	1.1110
Bonds		
	K_θ (kcal·mol^{-1}·rad^{-2})	θ_0 (degrees)
CA CA CA	40.000	120.00
HP CA CA	30.000	120.00
CT3 CA CA	45.800	122.30
HA3 CT3 CA	49.300	107.50
HA3 CT3 HA3	35.500	108.40
Urey-Bradley		
	K_{ub} (kcal·mol^{-1}·rad^{-2})	S_0 (Å)
CA CA CA	35.00	2.41620
HP CA CA	22.00	2.15250
HA3 CT3 HA3	5.40	1.80200
Dihedrals		
	K_{chi} (kcal·mol^{-1})	n (multiplicity)	δ (degrees)
CA CA CA CA	2.8000	2	180.00
HP CA CA CA	4.2000	2	180.00
HP CA CA HP	2.4000	2	180.00
CT3 CA CA CA	3.1000	2	180.00
HP CA CA CT3	4.2000	2	180.00
X CT3 CA X	0.0000	6	0.00

Table S4) Absolute minimum interaction energies and distances for the interactions of benzene with Helium and Neon and the rare gases.

Benzene + Helium						
	Energy			Distance		
Geom	Ab initio	Drude	C22	Ab initio	Drude	C22
1	-0.1692	-0.2088	-0.2082	3.5929	3.2400	3.2400
2	-0.1161	-0.1036	-0.0946	2.7680	2.6400	2.6800
3	-0.1817	-0.2183	-0.2180	3.5404	3.2300	3.2300
4	-0.1591	-0.1684	-0.1568	3.5396	3.3900	3.4200
5	-0.1502	-0.1874	-0.1861	3.5991	3.1800	3.1900
6	-0.3515	-0.2690	-0.2687	3.0592	3.1500	3.1500
Benzene + Neon						
	Energy			Distance		
Geom	Ab initio	Drude	C22	Ab initio	Drude	C22
1	-0.6657	-0.4317	-0.4245	3.3619	3.2800	3.2800
2	-0.6752	-0.4468	-0.4387	3.3658	3.2000	3.2000
3	-0.7438	-0.3380	-0.3156	3.4529	3.4400	3.4700
4	-0.6579	-0.3872	-0.3805	3.2990	3.2300	3.2300
5	-0.8064	-0.5495	-0.5395	3.2059	3.2000	3.2000

Interaction orientations are in Figure 1 of the main text.