Supporting Information For: Structural and Dynamic Heterogeneity of Deep Eutectic Solvents Composed of Choline Chloride and ortho-Phenol Derivatives

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Table S1: VFT parameters and adjusted R-square fitness fit to the form $\eta = \eta_0 \exp \frac{B}{T-T_0}$ for all simulated and experimental viscosities.

System	η_0	B	T_0	R^2
Phenol (exp)	0.5662	354.4	216.8	0.9997
Phenol (sim)	3.463E-3	1846	100.1	0.9987
Catechol (exp)	8.680E-3	1330	179.0	0.9947
Catechol (sim)	5.264E-3	2018	124.5	0.9731
o-Chlorophenol (exp)	0.3786	447.1	209.4	0.9993
o-Chlorophenol (sim)	3.789	107.6	264.3	0.9766
o-Cresol (exp)	0.05180	948.4	167.8	0.9983
o-Cresol (sim)	0.02290	1272	144.9	0.9660

Table S2: Melting temperature (T_m) and enthalpy of fusion ($\Delta_m h$) for the compounds experimentally used in this work

Compound	T_m **[K]**	$\Delta_m h$ **[kJ/mol]**	**Ref.**
Choline Chloride	597	4.3	?
Phenol	314	11.51	?
Catechol	377.1	21.99	95
o-Chlorophenol	283	12.52	?
o-Cresol	305.4	14.8	?

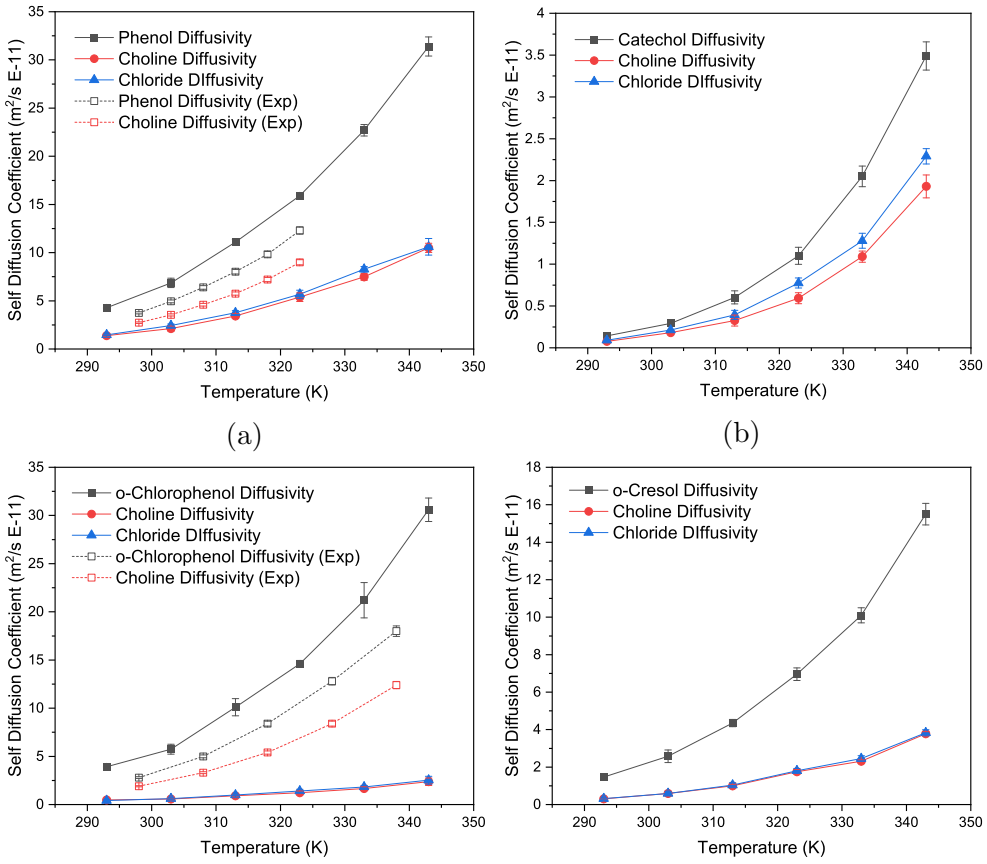


Figure S1: Self diffusion coefficients of the HBD, choline, and chloride in phenol (a), catechol (b), o-chlorophenol (c), and (d) o-cresol mixtures.

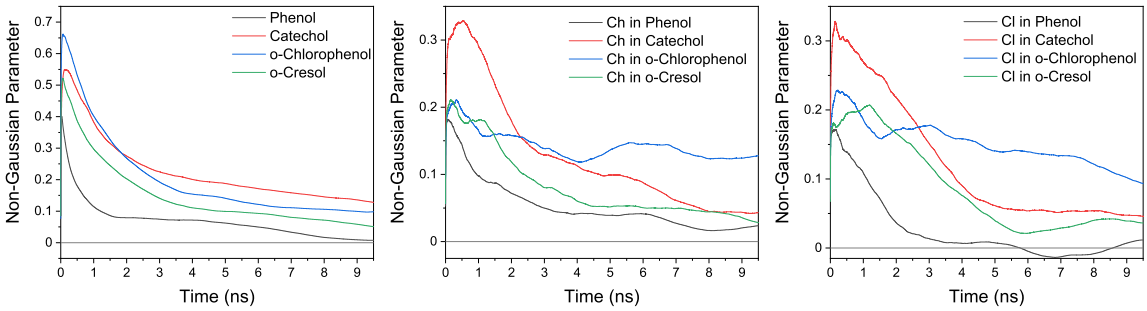


Figure S2: Non-Gaussian parameter of the HBD (a), choline (b), and chloride (c) within their respective mixtures at 333 K.

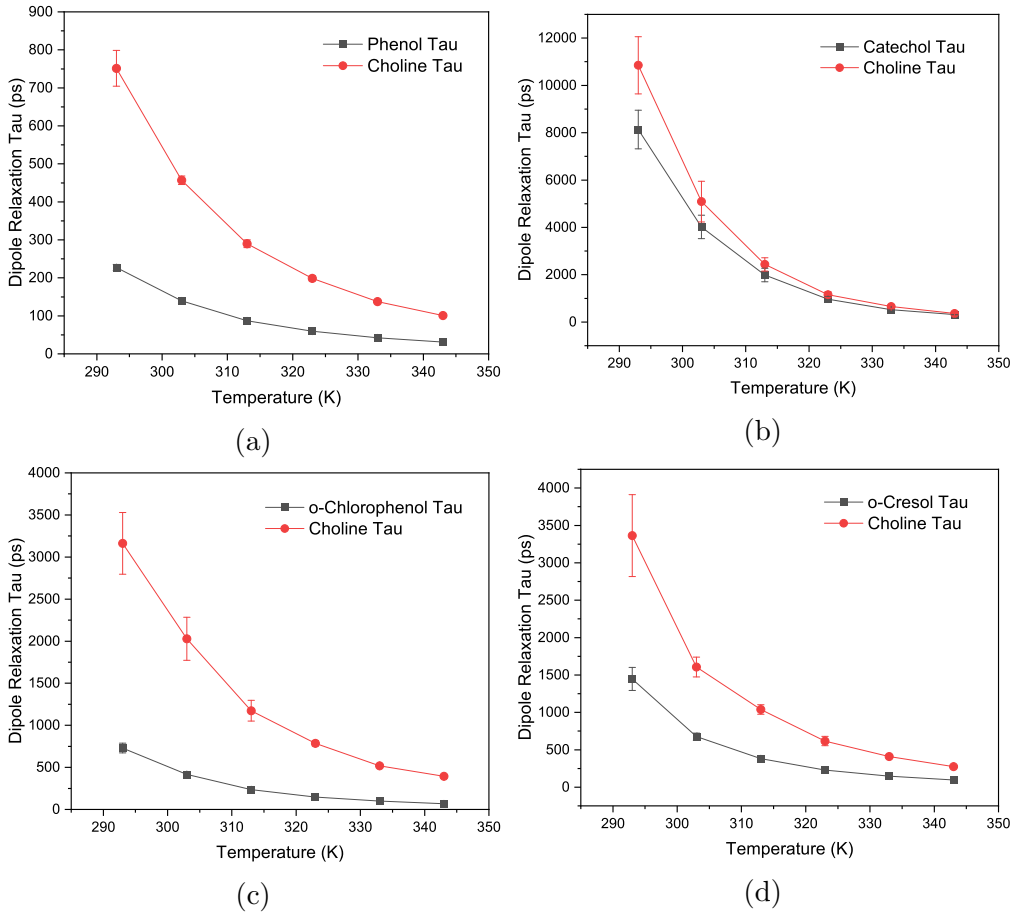


Figure S3: Simulated dipole relaxation correlation functions for phenol (a), catechol (b), o-chlorophenol (c), and o-cresol (d) mixtures.

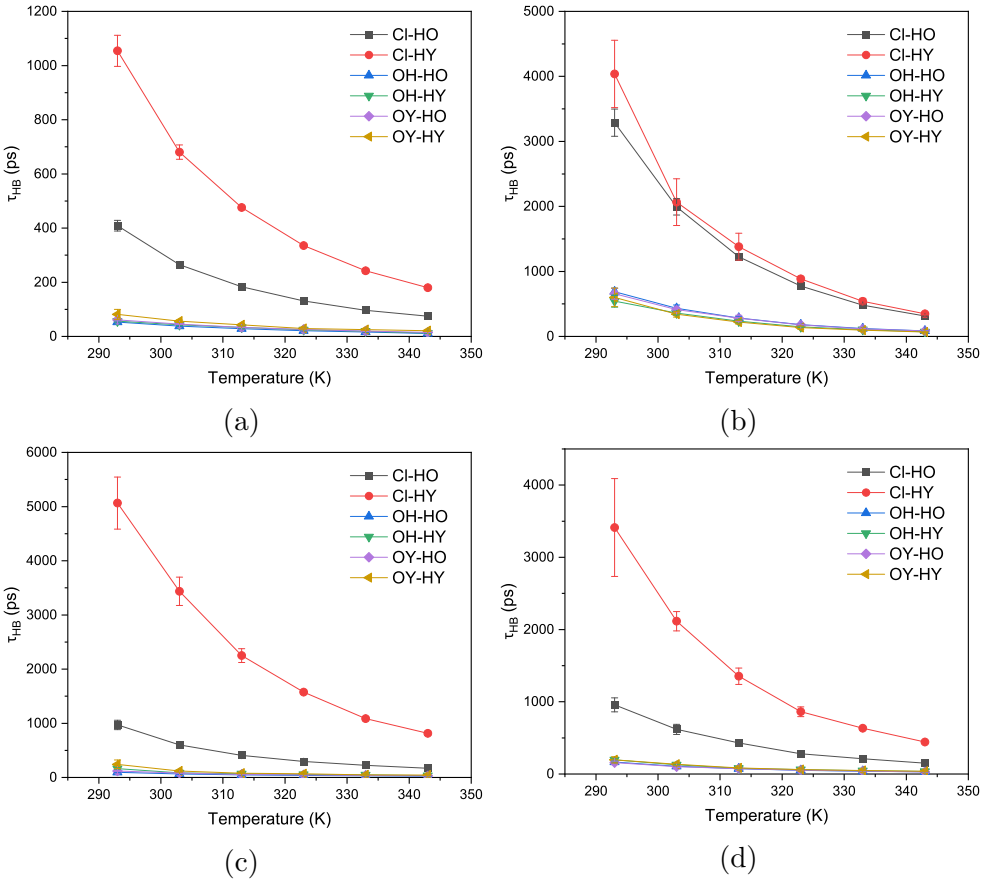


Figure S4: Average hydrogen bond lifetime of hydrogen bonding pairs in phenol (a), catechol (b), o-chlorophenol (c), and o-cresol (d) mixtures.

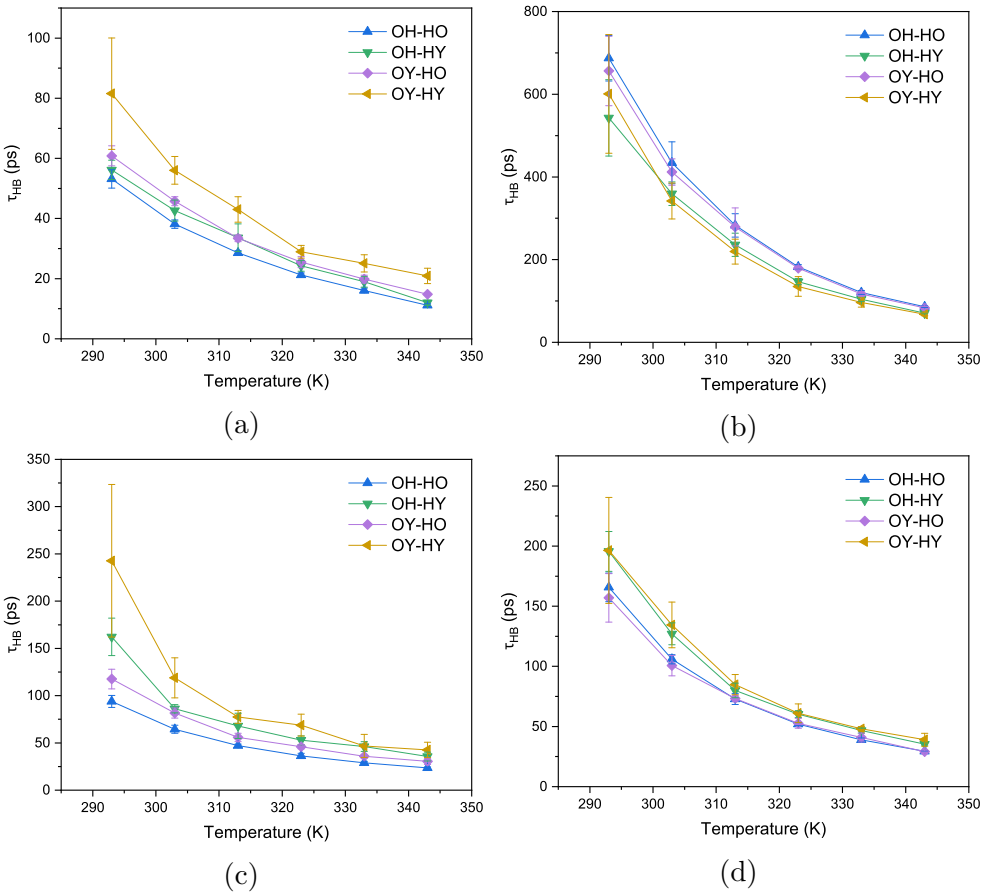


Figure S5: Average hydrogen bond lifetime of hydrogen bonding pairs excluding Cl-HO and Cl-HY in phenol (a), catechol (b), o-chlorophenol (c), and o-cresol (d) mixtures.

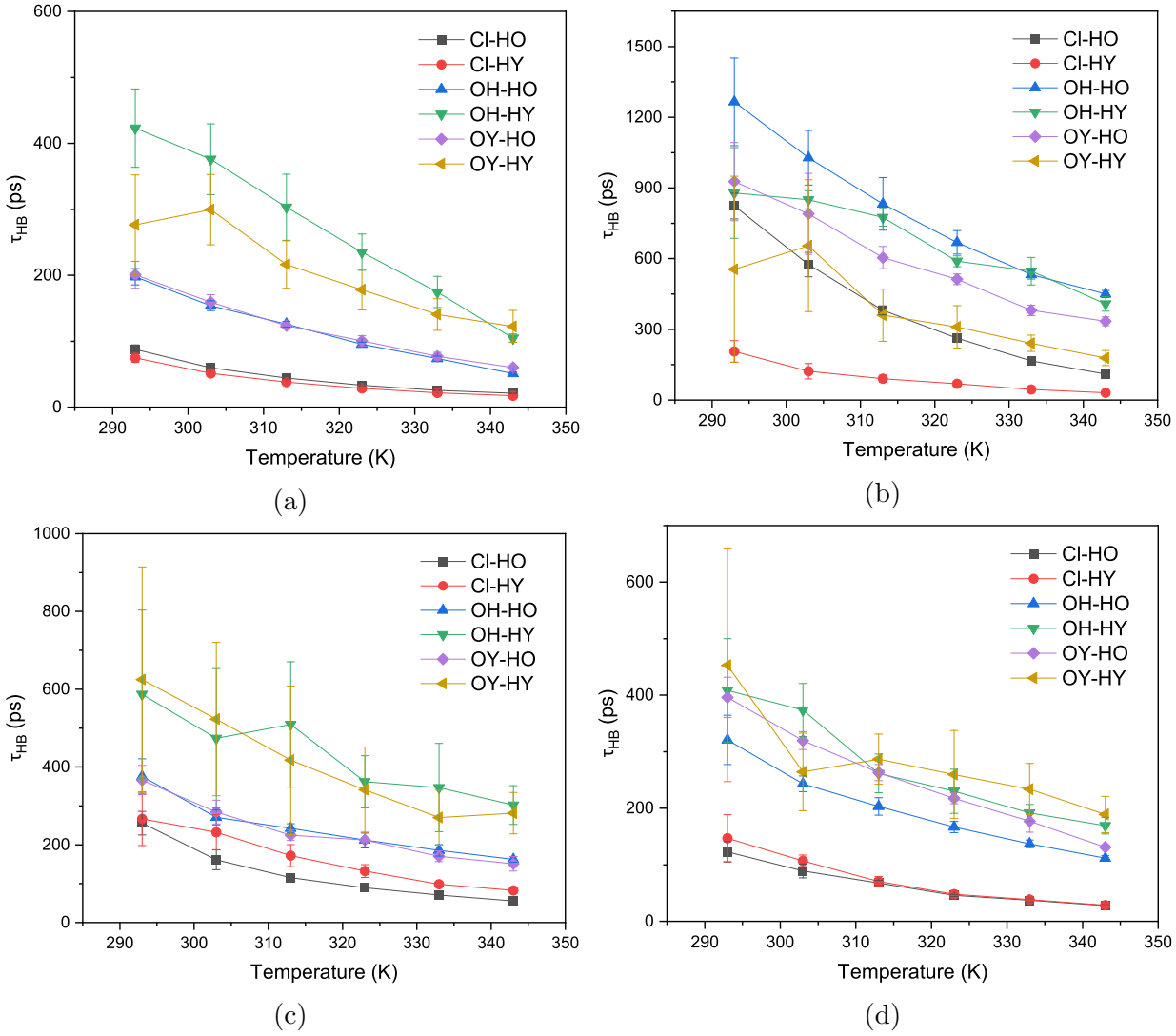


Figure S6: Average hydrogen bond reformation lifetime of hydrogen bonding pairs in phenoline (a), cateline (b), o-chlorophenoline (c), and o-cresoline (d).

Table S3: Table of standard deviations for coordination numbers of important interactions. Classical molecular dynamics (CMD) simulations were run at 303K and *ab initio* molecular dynamics (AIMD) simulations at 400 K. AIMD simulations of catechol were not performed due to the prohibitively long convergence times needed.

site-site	Phenol		Catechol		o-Chlorophenol		o-Cresol	
	CMD	AIMD	CMD	AIMD	CMD	AIMD	CMD	AIMD
Cl-HO	0.01	0.05	0.04	-	0.03	0.02	0.03	0.03
Cl-HY	0.001	0.05	0.01	-	0.001	0.05	0.003	0.05
OH-HO	0.002	0.03	0.01	-	0.002	0.01	0.01	0.04
OH-HY	0.0003	0.03	0.0004	-	0.0002	0.02	0.0007	0.01
OY-HO	0.001	0.01	0.004	-	0.004	0.06	0.002	0.07
OY-HY	0.0004	0.03	0.001	-	0.001	0.01	0.0006	0.02
Cl-N	0.02	0.07	0.05	-	0.02	0.02	0.02	0.04

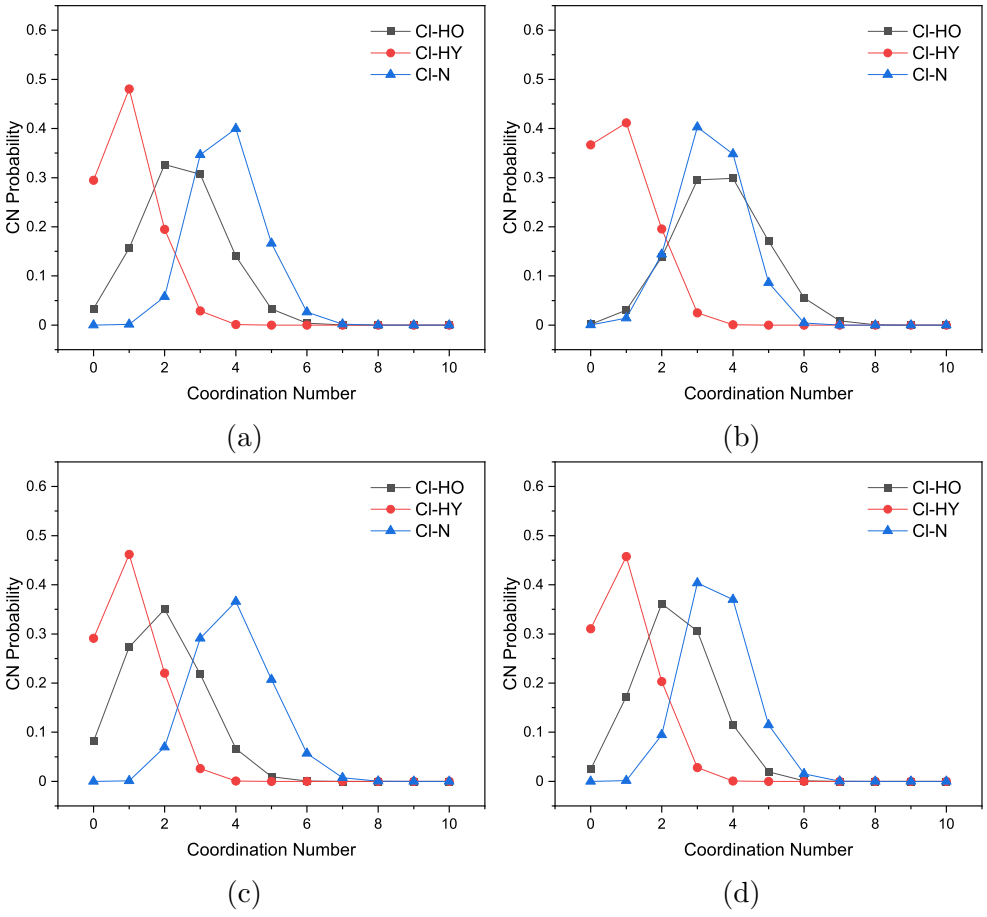


Figure S7: Chloride centered coordination number probabilities of chloride-HBD interactions at 303 K in phenol (a), catechol (b), o-chlorophenol (c), and o-cresol (d) mixtures.

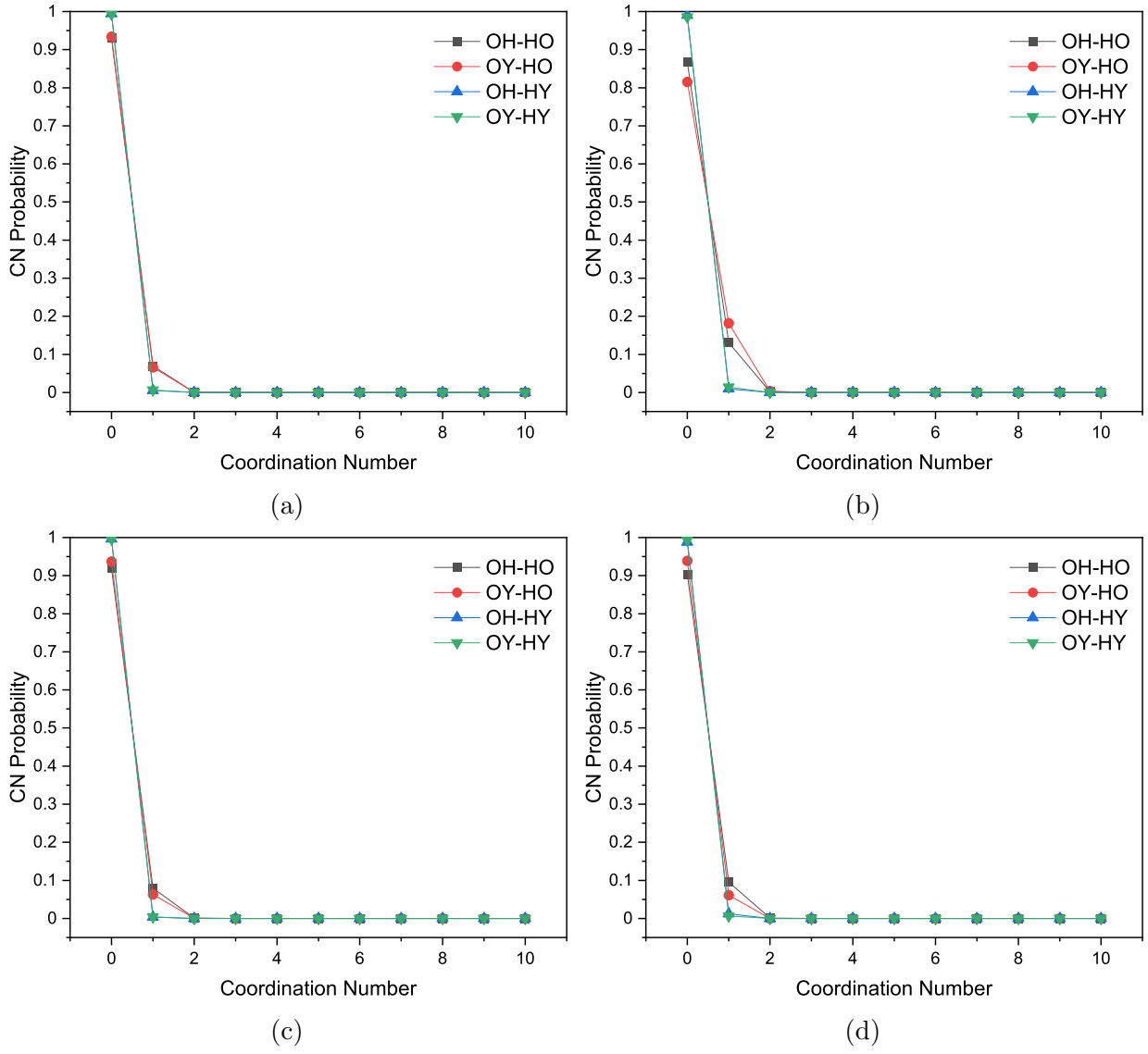


Figure S8: Chloride centered coordination number probabilities of chloride-HBD interactions in phenoline (a), cateline (b), o-chlorophenoline (c), and o-cresoline (d).

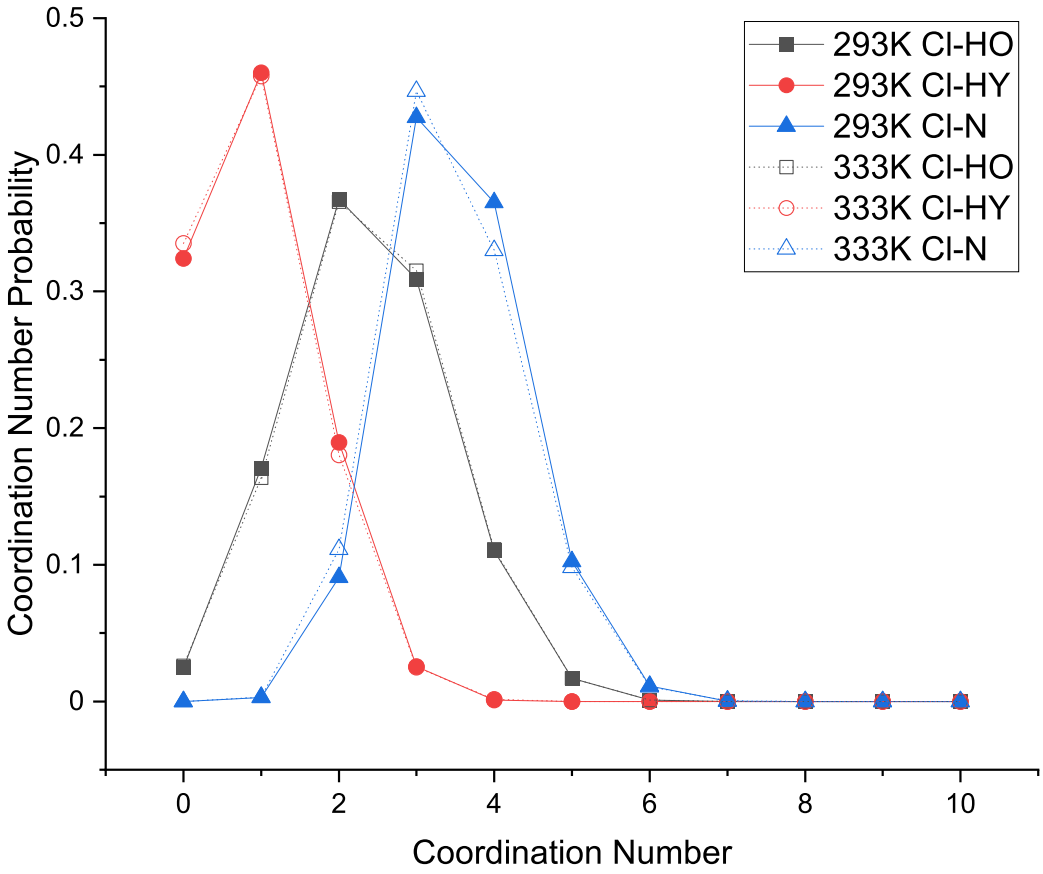
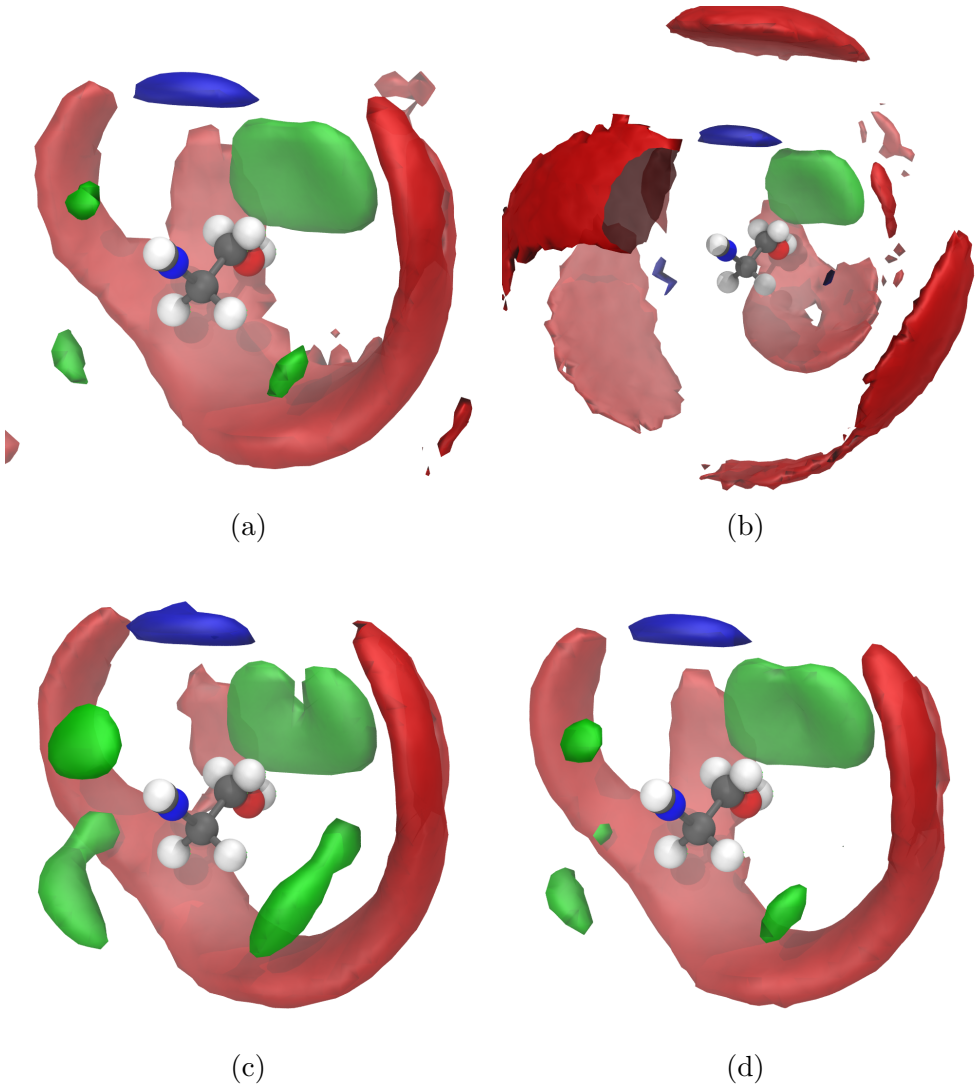


Figure S9: Coordination number probabilities of phenoline Cl coordinations. Indicates that the CN structure is invariant to temperature.



(a) (b)

(c) (d)

Figure S10: Choline centered molecular spatial distribution functions in phenol (a), catechol (b), o-chlorophenol (c), and o-cresol (d) mixtures.

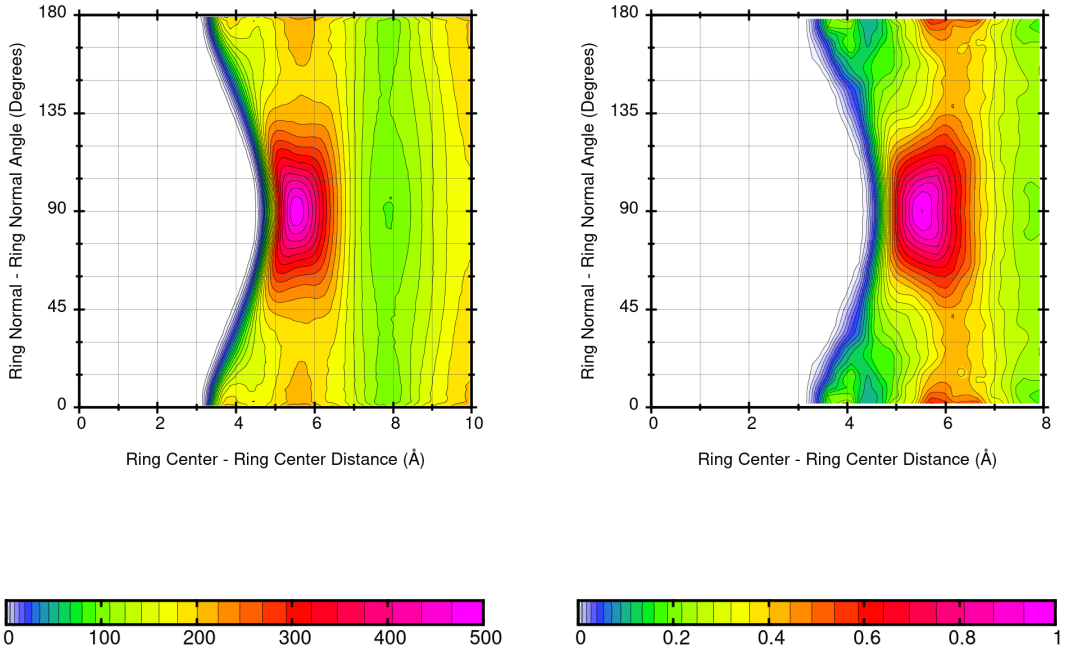


Figure S11: Comparison of CMD (left) and AIMD (right) CDFs of ring-ring structuring in 3:1 phenol:ChCl. Included below the CDFs are the heatmap legends in absolute counts for CMD and relative counts for AIMD.

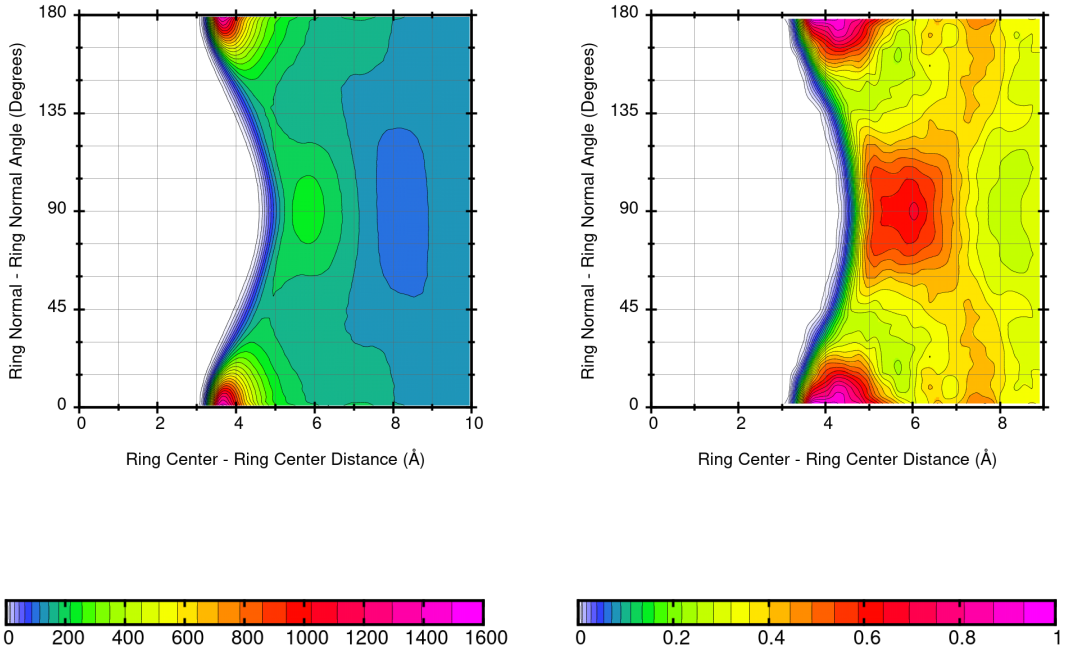


Figure S12: Comparison of CMD (left) and AIMD (right) CDFs of ring-ring structuring in 3:1 *o*-chlorophenol:ChCl. Included below the CDFs are the heatmap legends in absolute counts for CMD and relative counts for AIMD.

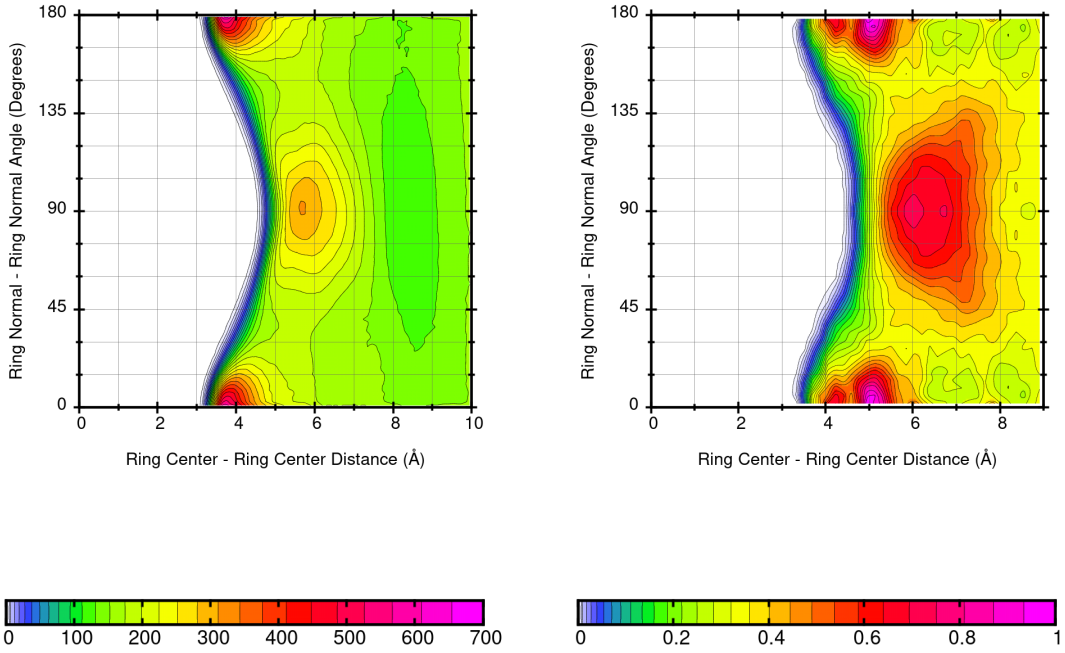


Figure S13: Comparison of CMD (left) and AIMD (right) CDFs of ring-ring structuring in 3:1 *o*-cresol:ChCl. Included below the CDFs are the heatmap legends in absolute counts for CMD and relative counts for AIMD.

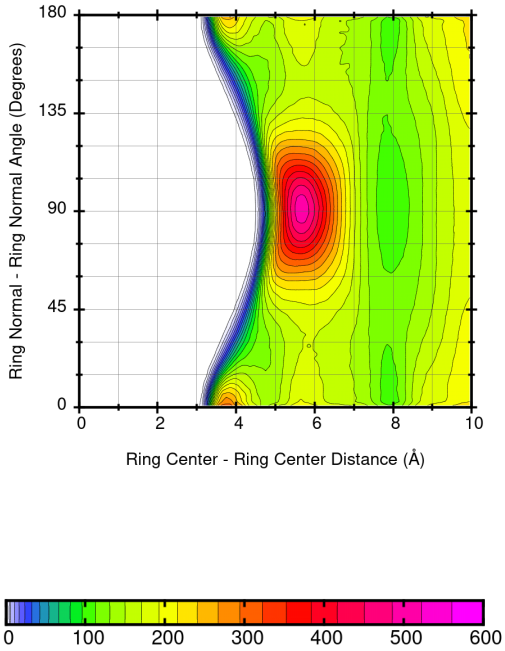


Figure S14: CDF of ring-ring structuring in 3:1 catechol:ChCl. Included below the CDF is the heatmap legend in absolute counts.

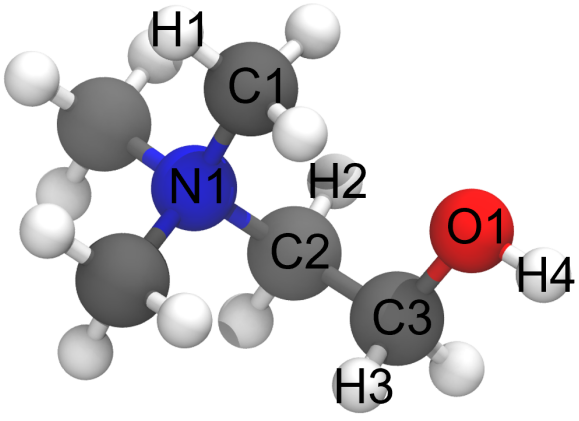


Figure S15: Labeled choline molecule.

Table S4: Choline chloride force field parameters. Note: Chloride ion CL1 not shown in above image.

Atom	Type	$q(e)$	σ(Å)	ϵ(kcal/mol)
C1	c3	-0.0940	3.400	0.1093
C2	c3	-0.0220	3.400	0.1093
C3	c3	0.1050	3.400	0.1093
N1	n4	0.0380	3.250	0.1699
O1	oh	-0.4330	3.066	0.2103
H1	hx	0.0830	1.960	0.0157
H2	hx	0.0780	1.960	0.0157
H3	h1	0.0360	2.471	0.0157
H4	ho	0.3190	0.112	0.0010
Cl1	cl	-0.7	4.400	0.0999

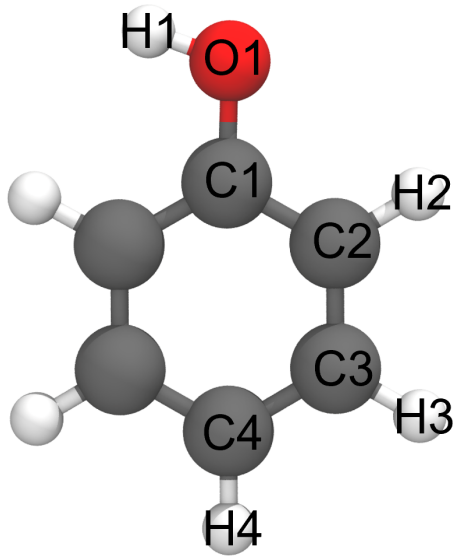


Figure S16: Labeled phenol molecule.

Table S5: Phenol force field parameters.

Atom	Type	$q(e)$	σ(Å)	ϵ(kcal/mol)
C1	ca	0.3360	3.400	0.0859
C2	ca	-0.2470	3.400	0.0859
C3	ca	-0.1100	3.400	0.0859
C4	ca	-0.1480	3.400	0.0859
O1	oh	-0.4710	3.066	0.2103
H1	ho	0.3260	0.000	0.0000
H2	ha	0.1520	2.600	0.0150
H3	ha	0.1250	2.600	0.0150
H4	ha	0.1170	2.600	0.0150

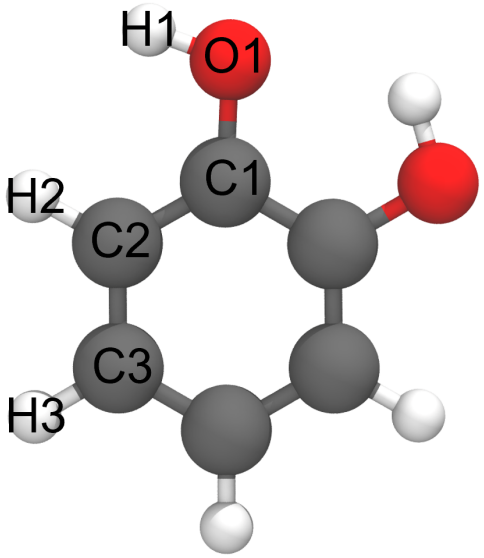


Figure S17: Labeled catechol molecule.

Table S6: Catechol force field parameters.

Atom	Type	$q(e)$	σ(Å)	ϵ(kcal/mol)
C1	ca	0.2460	3.400	0.0859
C2	ca	-0.2900	3.400	0.0859
C3	ca	-0.1850	3.400	0.0859
O1	oh	-0.5110	3.066	0.2103
H1	ho	0.3810	0.000	0.0000
H2	ha	0.1990	2.600	0.0150
H3	ha	0.1590	2.600	0.0150

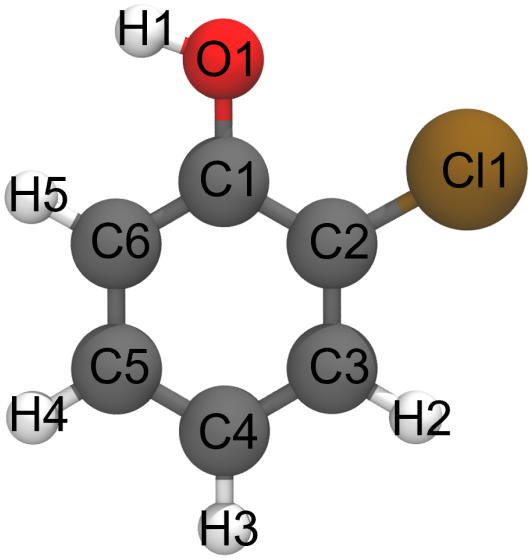


Figure S18: Labeled o-chlorophenol molecule.

Table S7: o-Chlorophenol force field parameters.

Atom	Type	$q(e)$	σ(Å)	ϵ(kcal/mol)
C1	ca	0.4490	3.400	0.0859
C2	ca	-0.1790	3.400	0.0859
C3	ca	-0.0010	3.400	0.0859
C4	ca	-0.2350	3.400	0.0859
C5	ca	-0.0740	3.400	0.0859
C6	ca	-0.2810	3.400	0.0859
O1	oh	-0.5320	3.066	0.2103
Cl1	cl	-0.0800	3.471	0.0999
H1	ho	0.3640	0.000	0.0000
H2	ha	0.1240	2.600	0.0150
H3	ha	0.1430	2.600	0.0150
H4	ha	0.1280	2.600	0.0150
H5	ha	0.1740	2.600	0.0150

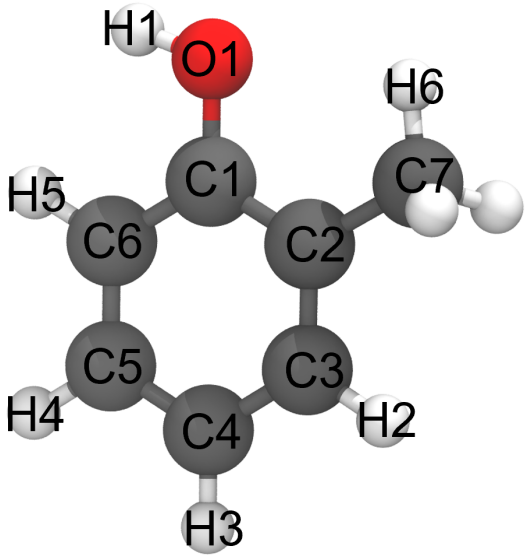


Figure S19: Labeled o-cresol molecule.

Table S8: o-Cresol force field parameters.

Atom	Type	$q(e)$	σ(Å)	ϵ(kcal/mol)
C1	ca	0.2690	3.400	0.0859
C2	ca	0.1380	3.400	0.0859
C3	ca	-0.2620	3.400	0.0859
C4	ca	-0.1260	3.400	0.0859
C5	ca	-0.1810	3.400	0.0859
C6	ca	-0.2080	3.400	0.0859
C7	c3	-0.3600	3.400	0.1093
O1	oh	-0.5510	3.066	0.2103
H1	ho	0.3900	0.000	0.0000
H2	ha	0.1510	2.600	0.0150
H3	ha	0.1240	2.600	0.0150
H4	ha	0.1400	2.600	0.0150
H5	ha	0.1670	2.600	0.0150
H6	hc	0.1030	2.650	0.0157

Example LAMMPS Input

The following input script outlines the overall format and settings followed for MD simulations conducted in LAMMPS. It follows the sequence of an NPT equilibration, re-sizing of the box, NVT production run, and finally a high thermo output viscosity run. While this is all in one input, any section can be easily adapted into a standalone input as needed.

```
# processors * * * grid numa
variable NAME index mol
variable mytemp index 293
units real
atom_style full
boundary p p p
pair_style lj/cut/coul/long 12
kspace_style pppm 1e-4
pair_modify tail yes
pair_modify mix arithmetic
special_bonds amber
bond_style harmonic
angle_style harmonic
dihedral_style charmm
improper_style cvff
neighbor 2.0 bin
neigh_modify delay 0 every 1 check yes page 1000000 one 20000
timestep 1.0
#—— read loose pack and run npt equil ————————-
read_data ph_1_chcl_3.data
```

```
velocity all create $mytemp 42321 units box
velocity all zero linear units box
dump NPTDUMP all custom 20000 npt.lammpstrj id type xu yu zu mol
log npt.log
dump_modify NPTDUMP sort id
minimize 1e-4 1e-6 10000 10000
fix NPT all npt temp $mytemp $mytemp 100.0 iso 1.0 1.0 100.0
fix dynbal all balance 1000 1.0 shift xyz 10 1.1
restart 50000 restart.npt.1 restart.npt.2
variable lx equal lx
variable ly equal ly
variable lz equal lz
fix 1 all ave/time 1000 1 1000 v_lx v_ly v_lz start 1000000 ave running
thermo_style custom step vol temp press ke pe etotal lx ly lz density f_1[1] f_1[2] f_1[3]
thermo 1000
run 2000000
write_restart restart.npt
write_data npt_restart.data
undump NPTDUMP
unfix NPT
unfix dynbal
#—- read equilibrated npt, adjust lxlylz to average of second half, run nvt——
change_box all x final 0.0 $(f_1[1]) y final 0.0 $(f_1[2]) z final 0.0 $(f_1[3]) remap
write_data nvtstart.data
unfix 1
reset_timestep 0
log nvt.log
```

```
dump NVTDUMP all custom 500 nvt.lammpstrj id type xu yu zu mol
dump_modify NVTDUMP sort id
thermo 1000
velocity all zero linear units box
fix NVT all nvt temp $mytemp $mytemp 100.0
restart 50000 restart.nvt.1 restart.nvt.2
thermo_style custom step vol temp press ke pe etotal
balance 1.0 x uniform y uniform z uniform
run 2000000
write_restart restart.nvt
write_data nvt_restart.data
undump NVTDUMP
unfix NVT
#— run viscosity type nvt ————————————-
reset_timestep 0 velocity all zero linear units box
dump VISCDUMP all custom 50000 visc.lammpstrj id type xu yu zu mol
log visc.log
thermo_style custom step vol temp press ke pe etotal density pxy pxz pyz pxx pyy pzz
thermo 5
fix VISCNVT all nvt temp $mytemp $mytemp 100.0
restart 50000 restart.visc.1 restart.visc.2
run 10000000
write_restart restart.visc
write_data visc_restart.data
```