



Supporting Information

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## Contribution of a solute's chiral solvent imprint to optical rotation.

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### *1. Experimental procedure*

Optical rotation ( $\alpha$ ) was measured with an AUTOPOL IV digital polarimeter. Optical rotation of (*S*)-methyloxirane (*Alfa Aesar*) in benzene, ortho-Xylene, meta-Xylene and 1,2,4 trimethyl benzene at 0.05 g/mL was measured at six different wavelengths. The specific rotation at a given wavelength  $[\alpha]_{\lambda}$  was calculated using:

$$[\alpha]_{\lambda} = \frac{\alpha V}{ml}$$

where,  $\alpha$  is the optical rotation in degrees,  $V$  is the volume ( $ml$ ) containing a mass  $m$  ( $g$ ) of the optically active substance, and  $l$  is the path length ( $dm$ ).

### *2. Monte Carlo simulation setup and procedure*

Monte Carlo (MC) simulations of (*S*)- and (*R*)-methyloxirane in a pre-equilibrated box of 500 benzene molecules were done using BOSS.<sup>[1]</sup> Simulations were done with a constant number of molecules at 25°c and 1 atm (NPT ensemble) with the Metropolis algorithm.<sup>[2]</sup> Calculations were performed with the periodic boundary condition, and long-range electrostatic interactions were evaluated by the Ewald method.<sup>[2]</sup> The OPLS-AA force field<sup>[3]</sup> with flexible solute and solvent geometries were used in the simulations. AM1<sup>[4]</sup>-

based CM1A<sup>[5]</sup> partial atomic charges scaled by 1.14 for the solute and solvent were used in the MC simulations. A more detailed description of the MC move and the atomic charge partitioning scheme can be found in [1].

### ***3. Calculation of optical rotation***

Structures from the MC trajectories were used for optical rotation (OR) calculations. Each structure had benzene molecules within a cut-off distance of 0.5 nm from the center-of-mass of methyloxirane. The total number of benzene molecules within the cut-off distance was 8-10. The specific rotation was averaged over an ensemble of 1000 structure snapshots at each wavelength to generate the ORD spectrum of (*S*)- and (*R*)-methyloxirane in benzene. Specific rotations for each structure were calculated according to the equation:

$$[\alpha]_{\lambda} = \frac{-1.34229 \times 10^{-4} \text{Tr}[G'(\omega)]\bar{\nu}^{-2}}{3M\omega}$$

where  $\text{Tr}[G(\omega)]$  is the trace of frequency dependent electric-dipole magnetic-dipole polarizability tensor,  $\bar{\nu}$  ( $=\lambda^{-1}=\omega/2\pi c$ ) is the radiation wavenumber, and  $M$  is the combined molar mass of methyloxirane and the number of solvent molecules in each snapshot. Thus, by including the mass of the benzene molecules we are properly normalizing  $[\alpha]_{\lambda}$  with respect to the total number of benzene molecules.  $[\alpha]_{\lambda}$  is an intensive property independent of the number of solvent molecules.

In the methyloxirane-benzene system the OR of the chiral solvent imprint (benzene cluster without the chiral solute) is comparable to the total OR of the system (solute + benzene; see Figure 2 in the manuscript). Figure 1S shows that the computed ORD spectra of the chiral solvent imprint with varied BP86/BLYP correlation-exchange functionals with the resolution of identity approximation (RI- $J$ )<sup>[6]</sup>, and SV/SVP/aug-cc-pVDZ basis sets are very similar. *Thus, ensemble averaged calculation of OR of chiral molecules in solution with varied functionals and basis sets gives similar results.*

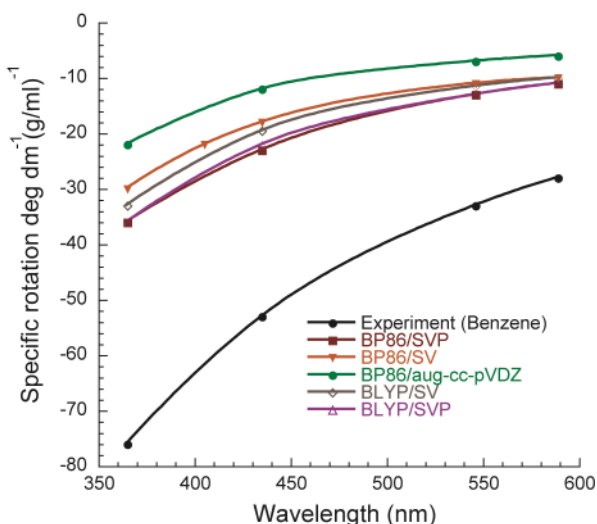


Figure 1S. Experimentally observed optical rotatory dispersion spectra (ORD) of (*S*)-methyloxirane in benzene and the computed ORD of the chiral solvent imprint (■ ▼ ● ◇ △). Calculations used varied TD-DFT/BP86/BLYP correlation-exchange functionals with RI- $J$  and SV/SVP/aug-cc-pVDZ basis sets. The specific rotation was averaged over 1000 structure snapshots from a monte-carlo simulation to generate the ORD of the chiral solvent structure.

In order to test the reliability of the methodology for computing the ORD of chiral molecules in solution we exemplify it by correctly predicting an averaged OR value close to zero for an achiral molecule in solution. Figure 2S shows the OR of an achiral ethylene oxide-benzene solution. The ORD was calculated using MC simulation and TD-DFT

(with BP86/aug-cc-pVDZ), as describe above for the methyloxirane-benzene system. The computed average ORD of ethylene oxide in benzene is close to zero, as expected.

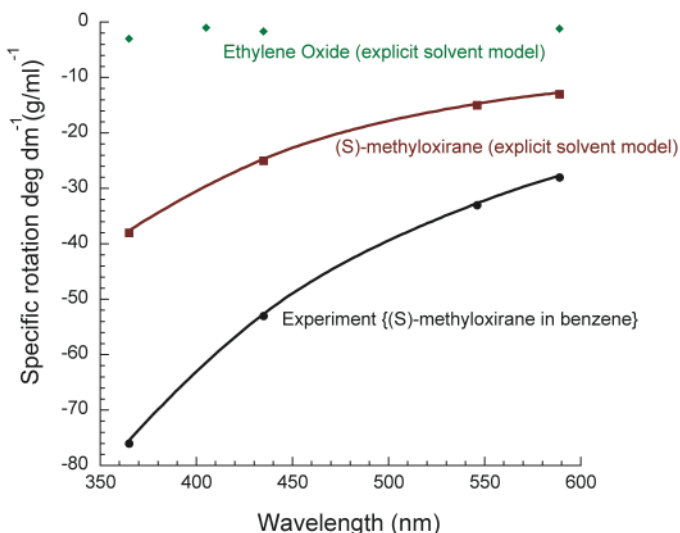


Figure 2S. Optical rotatory dispersion of ethylene oxide ( $\blacklozenge$ ) in benzene computed using explicit solvent model. Calculations used the TD-DFT/BP86 correlation-exchange functional with *RI-J* and aug-cc-pVDZ basis set. The specific rotation was averaged over 1000 structure snapshots from a monte carlo simulation to generate the ORD of ethylene oxide and (S)-methyloxirane ( $\blacksquare$ ) in benzene.

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