**Supplementary Material for:**

# Ground State Conformational Preferences
# and CH stretch-bend coupling in a
# Model Alkoxy Chain: 1,2-Diphenoxyethane

Evan G. Buchanan[†], Edwin L. Sibert III[‡]*, and Timothy S. Zwier[†]*

[†]Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084 U.S.A.
[‡]Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706 U.S.A.

1. Details of the IR population transfer method applied to DPOE.

2. A full listing of the calculated dihedral angles for the 26 conformers of DPOE (Table S1).

3. Discussion of the frequency scale factors chosen for DPOE relative to DPE.

4. Full author list for Ref. 55.

**1. Details of the IR population transfer method applied to DPOE:**

IR-population transfer spectroscopy is used here to determine the fractional abundances of the two conformers of DPOE. To make this measurement, the UV laser is fixed on a transition due to a single conformer and positioned to cross the supersonic free jet at $x/D = 6$, where x is the distance downstream of the nozzle orifice and D is the nozzle diameter. The infrared laser is positioned at an $x/D = 2.5$, upstream of the UV probe, and preceding the UV laser pulse by approximately 2 μs. In this manner, conformers have experienced a sufficient number of collisions with the backing gas to cool to the vibrational zero-point level before IR excitation; however, IR excitation occurs in a density regime where there are sufficient collisions following IR excitation to re-cool the vibrationally excited molecules back to the zero-point level before interrogation. Since IR excitation occurs to levels with energies above the barriers to isomerization, conformational isomerization can occur in competition with vibrational cooling. If an infrared transition due to conformer A is excited upstream, population will be transferred out of A to conformer B, leading to a net depletion in the population in A and gain in population in B. If an LIF transition due to A downstream, an IR depletion will be observed, while interrogation of B downstream will yield a gain at this same IR wavelength. IRPT scans are recorded with the IR operating at 10 Hz, and the UV laser at 20 Hz, using the active baseline subtraction mode of a gated integrator to record the difference in LIF signal from the UV laser with or without the IR present.

2. **Table S1:** Full listing of the calculated dihedral angles for the 26 conformers of DPOE.

| Conformer (Degeneracy) | $\varphi_1$ | $\theta_1$ | $\tau$ | $\theta_2$ | $\varphi_2$ | Relative Energy |
|---|---|---|---|---|---|---|
| i/ttt/i (1) | 180.0 | -180.0 | -180.0 | -180.0 | 0.0 | 0.000 |
| i/tg+t/i (2) | -1.8 | -177.9 | 71.6 | -177.9 | -1.8 | 2.670 |
| i/ttg-/i (2) | -179.4 | 178.1 | 178.9 | -81.2 | 179.5 | 5.558 |
| o+/g-g+t/i- (2) | 25.0 | -106.7 | 72.0 | -175.3 | -5.6 | 6.761 |
| o+/g+g-g+/o- (2) | 154.7 | 104.8 | -75.8 | 104.8 | -27.3 | 8.013 |
| i/tg-g-/i- (2) | -177.6 | 177.6 | -69.9 | -77.1 | -5.5 | 8.606 |
| o+/g+g+t/i (2) | 73.6 | 61.8 | 60.7 | -174.9 | -4.2 | 8.908 |
| i/g-g-g+/i- (2) | -2.4 | -79.4 | -71.8 | 100.2 | -11.8 | 10.615 |
| o+/g-g+g+/o+ (2) | 132.5 | -86.8 | 60.8 | 66.9 | 21.7 | 11.103 |
| i/g+tg-/i (1) | -178.4 | 80.4 | -180.0 | -80.4 | 178.4 | 11.573 |
| o+/g+tg+/i (2) | 47.8 | 73.7 | -176.9 | 79.7 | -175.4 | 11.762 |
| i/g-g-g-/i (2) | 176.4 | -77.1 | -70.2 | -77.1 | -4.4 | 14.165 |
| o-/g-g-g-/o+ (2) | -76.0 | -65.5 | -53.7 | -65.5 | 105.9 | 15.013 |
| i-/g+g+g+/o- (2) | -172.5 | 75.1 | 58.4 | 65.5 | -112.2 | 15.183 |

[*]Angles ranging between $-5° \leq \varphi_1/\varphi_2 \leq 5°$ are designated "i", $-5° > \varphi_1/\varphi_2 \geq -20°$ as "i-",
$5° < \varphi_1/\varphi_2 \leq 20°$ as "i+", $\varphi_1/\varphi_2 > 20°$ as "o+", and $\varphi_1/\varphi_2 < -20°$ as "o-".

## 3. Discussion of scale factors of DPOE relative to DPE:

In the present work, we have made one adjustment to the scaling factors described above. The spectra to the right in **Figure 6** were obtained by adjusting the position of the CH scissor overtones. We did this by scaling all modes other than the alkyl CH stretches by .989 as opposed to the .984 value used in the DPE work. The new value is that value obtained from fitting the mid IR data in **Table 2.** We subsequently varied $E_{anh}$, the anharmonicity of the local scissor modes, in order to fit the peak near 2980 cm^{-1} in the $C_{2h}$ ttt conformer DPOE spectrum. In contrast to DPE, the resonance interaction between the CH stretches and the scissor modes is almost negligible due to the higher frequencies of the scissors in DPOE. The transition at 2980 cm^{-1} is assigned as the overtone of the scissors mode. We again find $E_{anh} = 47$ cm[-1]. We believe

that such close agreement is fortuitous, given that the scaling factor for DPE was taken from 1,2

difluoroethane scissor calculations.

## 4. Full reference list for reference 55.

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision A.02, *Gaussian, Inc., Wallingford CT*. 2009.