Benzyldiene Malononitriles as Local Friction Probes

- Experimental Characterization
- Electronic Structure Calculations
- Simulations of Solution-Phase Dynamics

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“Push-Pull” “Molecular Rotors”

- significant CT character to $S_0 \rightarrow S_1$; large $\beta$
  $\mu_0 \sim 9$ D, $\mu_1 \sim 18$ D
- weakly fluorescent in most solvents
  $\phi_f \sim 10^{-3} - 10^{-4}$; $\tau_f \sim 1$ ps
- $S_1 \rightarrow S_0$ sensitive to local fluidity or free volume of environment
- used to probe liquids, polymers & biological systems*

Our Interests:
- determine deactivation mechanism & better define what is being sensed
- learn about reactive friction

Polymerization of MMA


Spectra & Solvatochromism

![Graphs showing spectral changes across different solvents and dielectric constants.]

- Vibronic widths in $S_1 > S_0$
- Absorption shifts indicate $\Delta \mu = 7-8$ D, consistent with electrochromism
- Emission shifts smaller than expected

fs-Time-Resolved Emission (25 °C)

Kerr Gated Emission of DMN

Intensity Decays (DMN)

Solvent | η/ cP | τ₀/ps | β | <τ> / ps
---|---|---|---|---
cyclohexane | 0.9 | 0.7 | 1 | 0.7
CH₃CN | 0.3 | 1.5 | 0.94 | 1.5
DMSO | 2 | 3.0 | 0.79 | 3.4
ethylene glycol | 17 | 3.9 | 0.75 | 4.6
[N₃p₃₁₁]⁺[Tf₂N⁻] | 113 | 2.5 | 0.63 | 3.5


Pacifichem 12/19/10
Heterogeneous Spectra & Kinetics in ILs

REE Shifts of Emission

- Red-edge shifts observed in slower solvents at RT (ILs, n-alcohols, ...)
- $\tau_{\text{rxn}}$ is also $\lambda_{\text{exc}}$ dependent: “dynamic heterogeneity”
can estimate reaction times \( \approx \) lifetimes from QYs if \( k_{rad} \) is known

\[
\tau_f^{-1} = k_{rad} (\varphi_f^{-1} - 1) \approx \tau_{rxn}^{-1}
\]

\( k_{rad} \) from time-resolved emission:

\[
k_{rad} = \frac{\varphi_f}{<\tau_f>}
\]

\( k_{rad} \) from absorption:

\[
k_{rad} / \text{s}^{-1} \approx 2.88 \times 10^{-9} n^2 (\tilde{\nu}_{em}^3 / \text{cm}^{-3})
\]

\[
\otimes \int_{s_i} \frac{\varepsilon(\nu)/ (\text{M}^{-1}\text{cm}^{-1})}{\nu} d\nu
\]

\( (\varphi_f \text{ difficult to measure}) \)

\( k_{rad} \text{ solvent independent} \)

\( M_{01}=M_{10}=6.6 \pm 0.2 \text{ D, the same for both solutes} \)
Survey of Reaction Rates

33 Solvents (25 °C)

\[ \ln(k_{\text{rxn}} / \text{s}^{-1}) \]

\[ \ln(\eta / \text{cP}) \]

- k(DMN) \sim 2k(J DMN)
- \[ k_{\text{rxn}} / T \propto \eta^{-p} \]

<table>
<thead>
<tr>
<th>Exp. p</th>
<th>DMN</th>
<th>J DMN</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-alkanes</td>
<td>.19</td>
<td>.29</td>
</tr>
<tr>
<td>n-alcohols</td>
<td>.14</td>
<td>.41</td>
</tr>
<tr>
<td>mTHF (T)</td>
<td>.69</td>
<td>.78</td>
</tr>
<tr>
<td>1-PrOH (T)</td>
<td>.39</td>
<td>--</td>
</tr>
</tbody>
</table>

solvent polarity?
What’s the Mechanism?

Loutfy (1982)  
Mqadmi (1990)  
Torkelson (1995)  
Drickamer (1998)  
Samanta (2008)  
Haidekker (2009)

DCVJ - A Molecular Rotor

Electron Donor  
Ex: 460 nm (blue)  
Em: 505 nm (green)

Electron Acceptor
Gas-Phase Torsional PES of $S_1$ DMN

- $\tau_c$ is primary reaction coordinate
- scanned at SA2-CAS(12,11)/6-31G(d) level ($S_0$ optimized geometries)

Details of PES Search

- search of $S_1$ @ RI-CC2/def2-TZVP level located minima at $\tau_a=90^\circ$ and $\tau_b\sim\tau_c\sim20^\circ$, but no $\tau_b=90^\circ$ TICT state
- (a TD-B3LYP located a $\tau_b$ TICT state, but LC corrections eliminated it)
- a CIS search did not reveal a $\tau_b$ TICT state; instead a conical intersection with $S_0$ was found at $\tau_c=90^\circ$

CAS-SCF Predictions

- $E$ / kJ mol$^{-1}$ vs. $\tau_c$ / degree
- Dipole Moments $\mu_0$, $\mu_1$, $M_{01}$
- $S_0$, $S_1$, Expt.
Preliminary MD Simulations

- explore solvent effect by combining QM E(τ_c) with classical solvent bath via molecular dynamics simulations
- semi-rigid solute (τ_c only)
- 108 CH₃CN solvent molecules
- 2000 n.e. trajectories on U₁
- terminate when |τ_c| = 85°
Variations with $\tau_c$ PES & Solvent

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**S$_1$ Potentials & Their Dynamics**

- $E_{rel}/kJ \cdot mol^{-1}$
- $\tau_c / \text{degree}$

**Viscosity Dependence**

- $\tau_{rxn} \propto \eta^{0.6}$
- "Relative Viscosity"

- Dynamics are sensitive to $k_B T$-level variations in $E(\tau_c)$
- Viscosity variation & DMN/JDMN difference like experiment
- Overall approach is promising
DMN and JDMN characterized as environmental probes
- first direct measurements of room-T dynamics
- $k_{rad}$ conveniently independent of solvent

$\varphi_f \leftrightarrow \tau_{rxn}$ data in 33 common solvents:
- observe $k_{rxn}/T \propto \eta^{-p}$ with $0.2 < p < 1$ in single solvents vs. $T$
  & in homologous series
- analogous to small-molecule rotations
- solvent polarity likely important

$S_1$ decays primarily via double-bond isomerization ($\tau_c$)

initial MM simulations on QM-derived $\tau_c$ surfaces exhibit proper time scale and sensitivity to solvent & solute comparable to experiment

further simulations should provide molecular-level description of environmental friction on these reactions
Acknowledgements

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