Fluorescence Depolarization in Molecular Gyroscopes: Evidence of a Photonic Brake.

Carlos N. Sanrame, Ignacio B. Martini, Zaira J. Dominguez, Benjamin J. Schwartz* and Miguel A. Garcia-Garibay*

Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095-1569.

RECEIVED DATE (automatically inserted by publisher); schwartz@chem.ucla.edu; mgg@chem.ucla.edu

We recently reported the design, construction, and dynamics of crystalline solids built with molecules having structures and properties analogous to those of macroscopic compasses and gyroscopes.1 As illustrated in Scheme 1, they consist of a 1,4-diethynylbenzene linked to triarylmethanes1 or triptycenes.2

Scheme 1

![Scheme 1 diagram]

Our interest in molecular compasses and gyroscopes stems from their potential in the fabrication of ultrastable electro-optic materials.3 Ideally, the response of their reorienting dipoles to external fields should result in tunable birefringence, dichroism, and nonlinear optical effects. Indeed, rotation about alkyn-aryl sigma bonds is known to be barrierless in the gas phase,4 and examples of such bonds in crystals with ground-state rotational time constants of less than 100 ns at 300K (e.g., 1b)5b bode well for the construction of nearly frictionless rotating units in solids.

In an attempt to measure their gyroscopic motion in their lowest electronic excited state, we decided to explore the fluorescence depolarization of the molecules in Scheme 1 in solution with the hope of extending later to the solid state. The idea was to directly measure the rotational diffusion of the central phenylene group by exciting the molecule with polarized light, and collecting the emission from a state whose transition dipole has a component perpendicular to the alkyn bonds (along the z-axis in Scheme 1).5 However, instead of a rapid depolarization consistent with rotation of the central phenylene, we observed a much slower process consistent with rotation of the entire molecule. Based on this and known changes in the excited-state bond order,6 we propose that electronic excitation causes a stoppage of the gyroscopic rotation about the original alkyn-arene single bonds in what can be thought of as a “photonic brake”.7

To analyze the rotational correlation times, experiments were carried out with 10−3 M solutions in solvents of different viscosity: methyl cyclohexane (MCH), CH3Cl, and mineral oil.8 The UV-Vis and fluorescence spectra of compounds 1a and 2 are essentially identical to those of the corresponding 1,4-diethynylarenes.9 It has been suggested that the weak fluorescence of p-diethynylbenzene results from mixing the symmetry-allowed S1 (B1g) state with a small amount of the symmetry-forbidden S1 (B2g) state.10

Figure 1. (Top) Fluorescence dynamics of 1a following polarized excitation at 293 nm with excitation and detection polarized either parallel (blue) or perpendicular (red) to each other. (Bottom) Anisotropy decay (Eq. 1, green) and single-exponential fit (cyan).

The main effect of the -F and -CN substituents is to add oscillator strength to the otherwise forbidden S1 transition and to increase the fluorescence quantum yield and lifetime in CH3Cl, from [I]0=0.05 and [I]=0.32 ns in 1a to [I]=0.44 and [I]=1.6 ns in 3 (see Table 1). The emission maxima of 1a, 2, and 3 occur at 315, 317, and 339 nm, respectively. Our hope was that the substituents would cause the transition dipoles of 2 and 3 to lie closer to the z-axis than that of compound 1a. However, what we will see below is that the emission dipole moments of all three molecules are rotated by ~24° with respect to the absorption dipole.
of Figure 1 shows that the anisotropy decay of 1a in CH₃Cl, decays exponentially with a time constant \( \Gamma = 170 \pm 20 \) ps. The fact that the anisotropy decays fit well to single exponentials indicates that there is only one dominant rotational motion in the excited state. Initially this came as a surprise given that we expected a fast anisotropy decay due to the gyroscopic motion of the central phenylene unit, followed by slower decays resulting from rotational diffusion about the shorter and longer molecular axes of this prolate-spheroidal molecular top.

To better understand the observed anisotropy decays, we analyzed the effects of solvent viscosity on the kinetics of depolarization using a Stokes-Debye-Einstein model, where \( \Gamma = 4 \pi a^3 k_b T / 3 \eta \) Eq. 2

Table 1. Fluorescence lifetimes and anisotropy decay parameters from compounds 1a, 2, and 3.

<table>
<thead>
<tr>
<th>CH₃Cl (( \Gamma = 0.44^\text{a} ))</th>
<th>MCH (( \Gamma = 0.74^\text{a} ))</th>
<th>Mineral Oil (( \Gamma = 29^\text{a} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Free Rotor</td>
<td>Lifetime</td>
</tr>
<tr>
<td></td>
<td>[1] (ps)</td>
<td>( \Gamma^b ) (ns)</td>
</tr>
<tr>
<td>1a</td>
<td>6.5^d</td>
<td>0.32±0.05</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>17.4±0.5</td>
</tr>
<tr>
<td>3</td>
<td>1.6±0.15</td>
<td>0.28</td>
</tr>
</tbody>
</table>

\( ^a \) No fast decay was observed within \( \approx 10 \) ps resolution. \( ^b \) Single exponential. \( ^c \) Error in \( r(0) \) is 0.05. \( ^d \) Values calculated with eq. 2. \( ^e \) Values calculated as in ref. 13. \( ^f \) Assuming the dimensions of diethylbenzene. \( ^g \) Viscosities from reference 8.

The fact that 2 and 3 give identical results (within experimental error) to 1a confirms that there are no rotation processes that occur faster than our time resolution. The fact that \( r(0) = 0.28 \) thus requires the emission dipole to lie in three molecules to be rotated by \( \approx 24^\circ \) relative to the absorption dipole. A change of this type is what might be expected for an electronic excitation accompanied by strong vibronic coupling with in-plane deformation between the ring and the trityl groups, deformation of the acetylenic triple bond, and an in-plane ring deformation, as suggested by Laposa. In addition, well-known changes in bond order suggest a bisallenic excited state, as illustrated in Scheme 2. Put together, the results suggest that excitation of molecular compasses based on di-alkynylphenylene rotors arrest the free rotation of the ground state. Mechanisms such as these may become the basis of photonic braking in artificial molecular machines, allowing non-linear optical or other thermally activated gyroscopic processes to be switched off at will.

Acknowledgment.

This work was supported by NSF grants DMR-0307028 (MAGG) and DMR-0305254 (BJS), and by ACS PRF grant 37029-AC57 (BJS). BJS is a Camille Dreyfus Teacher-Scholar.


13. The free rotor times were calculated from \( \gamma = (2/\sqrt{9})(1/kT) \); See: Kawski, A. Crit. Rev. Anal. Chem. 1993, 23, 459-529.