Fluorescence Quenching of Carbonyl-Twisted 5-Acyl-1-dimethylaminonaphthalenes by Alcohols

Rachel S. Anderson, Newton V. Nagirimadugu, and Christopher J. Abelt*

Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23185, United States

Supporting Information

ABSTRACT: Derivatives of 1-dimethylamino-5-propionynaphthalene that constrain the carbonyl group into a five-, six-, and seven-membered ring were prepared, and their fluorescence quenching in protic solvents was studied. Evidence for enhanced quenching due to carbonyl twisting out of the molecular plane is presented, but this effect is heavily masked by the strong quenching by all of the derivatives and by the ring size-dependent deactivation seen in polar, aprotic solvents. Calculations show strong, ring size-dependent vibrational coupling between the carbonyl group and the naphthalene ring in the first excited state.

INTRODUCTION

Naphthalene derivatives bearing a widely spaced electron-accepting carbonyl group and a dialkylamino electron-donating group show charge-transfer excited state emission. The archetypal member of this set is 6-propionyl-2-dimethylaminonaphthalene (2,6-Prodan).1 Because charge transfer gives rise to a large excited state dipole moment, its emission shows strong solvatochromism.2−5 In addition, its emission is slightly quenched in methanol (23% reduction). Constraining the carbonyl group in a six-membered ring has no significant effect on the methanol quenching (25%).6 However, if the carbonyl group is in a seven-membered ring, the emission is strongly quenched (84%) in methanol. A similarly strong quenching effect was observed for 6-pivaloyl-2-dimethylaminonaphthalene.7 The carbonyl group is forced out of the molecular plane in the latter two compounds. The enhanced quenching was ascribed to the enforced out-of-plane twisting of the carbonyl group.

The Prodan regioisomer having the donor and acceptor groups in the 1,5-positions is very similar to 2,6-Prodan.1 Unlike 2,6-Prodan, the emission of the 1,5-isomer shows much stronger quenching in methanol (98%). This paper examines the relationship between twisting of the carbonyl group on the fluorescence quenching in protic solvents for a set of four 1,5-Prodan compounds: the parent structure (1) and three derivatives where the carbonyl is in a five-, six- and seven-membered ring (2−4) (Figure 1).

RESULTS

Preparation of 1,5-Prodan Ring Derivatives. Ring derivatives 2−4 are prepared as shown in Scheme 1. The requisite number of atoms for each ring was appended by the Negishi coupling with intermediate S. Intramolecular electrophilic acylation created the ring structures. For 2 and 3, the cyclization was accomplished using polyphosphoric acid with the ethyl esters. For 3, the cyclization did not go to completion, and unreacted ester was removed by saponification. The polyphosphoric acid method failed in the case of 4. Cyclization required more forcing conditions: using the acid chloride as the reactant and aluminum trichloride as the promoter. The precursor to all three compounds is compound S, obtained by methylation of the corresponding primary amine. While S is commercially available, it was prepared in seven steps from 6-bromo-2-naphthol by the route described in the Supporting Information.

Photophysical Studies. The four compounds show one absorption band above 300 nm. The maximum absorption wavelength for each varies by no more than 3 nm in different solvents (e.g., toluene, ethyl acetate, and methanol). For 1 and 4, the absorptions are centered at 332 and 330 nm, while for 2 and 3, they are redshifted to 355 and 351 nm. The position of the absorption band is related to the twisting of the carbonyl group. Compound 2 with the coplanar carbonyl group shows the longest wavelength absorption band, whereas compound 4 with the most twisted carbonyl group (vide infra) shows the shortest.

The relative quantum yields for 1−4 were determined in toluene using anthracene (Φ = 0.30) as a reference. They are 0.42 ± 0.03, 0.64 ± 0.03, 0.56 ± 0.01, and 0.43 ± 0.02, indicating that all are strong fluorophores. Quantum yields are the largest in chlorobenzene (0.44, 0.75, 0.59, and 0.52) and...
decrease as the solvent polarity increases for the aprotic solvents (Table 1). In acetonitrile, they have all decreased from the maximum values by roughly two-thirds. But in the case of 2, the decrease is only by 50%, while for 1, 3, and 4, they are 70, 68, and 73%, respectively.

All of the four exhibit strong solvatochromism in their emission spectra (Table 1).

The fluorescence maxima successively shift to higher wavelengths as the solvent polarity increases as a result of the charge-transfer nature of the excited states. The fluorescence spectra in the various solvents are presented in the Supporting Information (Figures S1–S4). Plots of the fluorescence center-of-mass versus the $E_T(30)$ solvent polarity parameter are shown in Figure 2. The slopes of these plots are a measure of the degree of charge transfer in the relaxed excited state. For these four compounds, the slopes are close in magnitude (−151, −153, −124, and −133) suggesting similar degrees of charge transfer in the relaxed excited states. The plot for the five-membered ring (2) shows a consistent displacement to shorter wavelength emission values.

The fluorescence of 1–4 is strongly quenched by protic solvents. In going from acetonitrile to isopropanol, the

| solvent | 1     | 2     | 3     | 4     |
|---------|-------|-------|-------|-------|
| Cyc     | 0.32  | 0.52  | 0.22  | 0.15  |
| Tol     | 0.42  | 0.64  | 0.56  | 0.43  |
| PhCl    | 0.44  | 0.75  | 0.59  | 0.52  |
| CH$_2$Cl$_2$ | 0.33 | 0.65  | 0.49  | 0.42  |
| EtOAc   | 0.24  | 0.46  | 0.31  | 0.22  |
| Et$_2$O | 0.35  | 0.56  | 0.39  | 0.25  |
| Me$_2$CO | 0.18 | 0.41  | 0.27  | 0.21  |
| MeCN    | 0.13  | 0.37  | 0.19  | 0.14  |
| DMSO    | 0.12  | 0.45  | 0.22  | 0.19  |
| iPrOH   | 0.021 | 0.16  | 0.030 | 0.018 |
| BuOH    | 0.018 | 0.15  | 0.033 | 0.015 |
| PrOH    | 0.014 | 0.12  | 0.027 | 0.011 |
| EtOH    | 0.010 | 0.085 | 0.018 | 0.007 |
| MeOH    | 0.003 | 0.040 | 0.009 | 0.002 |

“Solvents are cyclohexane, toluene, chlorobenzene, dichloromethane, ethyl acetate, diethyl ether, acetone, acetonitrile, dimethyl sulfoxide, isopropanol, butanol, propanol, ethanol, and methanol.
quantum yields decrease by factors of 84, 57, 84, and 87%. These decreases occur despite the fact that isopropanol is less polar than acetonitrile (Kamlet–Taft $\pi^*$ values of 0.48 vs 0.75). The decreases in the quantum yields are accompanied by redshifts in the fluorescence maxima due to H-bonding of the carbonyl group with the protic solvents in the excited state. The ring size has a strong influence on the H-bond-induced quenching. The slopes of the plots of the quenching magnitude (defined as the log of $I_{\text{toluene}}/I_{\text{solvent}}$) versus the solvent acidity (H-bond donating ability) are a measure of the degree to which H-bond formation from the protic solvent to the carbonyl oxygen in the excited state creates an efficient deactivation pathway to the ground state. The plots for 1–4 are shown in Figure 3. The slopes and standard deviations from duplicate determinations are in descending order: $2.96 \pm 0.05$ (4), $2.77 \pm 0.03$ (1), $2.18 \pm 0.01$ (3), and $1.92 \pm 0.01$ (2). This relative ordering is also manifested in the quantum yields in the protic solvents in Table 1.

**Computational Studies.** The electronic structures of the ground and first excited states were calculated with Gaussian 16. The calculations not only provided the degree of twist of the carbonyl group out of the molecular plane, but they also characterized the energy well of the twisting coordinate surrounding the optimum twist angle. The results are shown in Figure 4. Both 1 and 4 have significantly twisted carbonyl groups in the ground state ($137^\circ$ and $139^\circ$). Not surprisingly, the calculations show that 2 has a coplanar carbonyl group. For the six-membered ring (3), the carbonyl group is slightly twisted ($166^\circ$). The wells are steep for 2 and 4 and broad for the acyclic parent (1). In the excited state, the energy minima shift toward coplanarity for 1 and 4 but more so for the former ($170^\circ$) than the latter ($146^\circ$). The wells are steeper in the excited state. For 1, there is another minimum nearer the $0^\circ$ dihedral angle (not shown), but it is slightly higher in energy.

The dimethylamino groups show similar structural behavior for all four compounds, and this behavior for 1 was noted in our previous study. The dimethylamino groups are twisted out of plane by $47^\circ$ (average of two cisoid dihedral angles) in the ground state. In the excited state, they twist toward planarity ($\sim 33^\circ$), and the amino groups become less pyramidal. The nitrogens become more positively charged in the excited state ($-0.17 \rightarrow +0.33$) as a result of the charge transfer. The dipole moments increase from an average of 5.0 to 7.5 D.

The long wavelength absorption is calculated to be a relatively straightforward HOMO $\rightarrow$ LUMO electronic transition. These frontier molecular orbitals are shown in Figure 5 for compound 4. The amino n orbital significantly contributes to the HOMO, while the carbonyl $\pi^*$ orbital...

---

**Figure 3.** Plots of $\log(I_{\text{toluene}}/I_{\text{solvent}})$ vs SA for 1 (red box, red dashed line), 2 (blue circle, blue dashed line), 3 (green triangle up open, green dashed line), and 4 (violet diamond open, violet solid line). Solvents (SA values) are 2-octanol (0.09), 2-butanol (0.22), cyclopentanol (0.26), 2-propanol (0.28), 1-pentanol (0.32), 1-butanol (0.34), 1-propanol (0.37), ethanol (0.40), and methanol (0.61).

**Figure 4.** Plots of potential energy vs dihedral angle for 1 (red box, red dashed line), 2 (blue circle, blue dashed line), 3 (green triangle up open, green dashed line), and 4 (black diamond open, black solid line) in the ground (bottom) and first excited states (top).
of the carbonyl oxygen are the symmetric and antisymmetric W modes, where there is significant coupling to the C6—C7 bond. For 2–4, the greatest displacement is seen in the symmetric stretching (sW), whereas for 1, it is in the antisymmetric mode (aW). The averages of the sW and aW frequencies decrease with increasing ring size for 2–4, but the average for 1 has an intermediate value (1580, 1606, 1577, and 1526 cm⁻¹). This result is consistent with the nearly identical carbonyl-twisting angles for 1 and 3 in the excited state.

## DISCUSSION

The photophysical behavior of 1–4 is best presented as a contrast to the behavior of the related 2,6-Prodan derivatives 6–9 (Figure 7). The first point of difference between the 1,5-Prodan derivatives and the 2,6-derivatives is that the former shows strong quenching in protic solvents, while for the latter, quenching is strong only for certain structures. The slopes of the plots of quenching magnitude versus solvent acidity (cf. Figure 3) are 0.74, 2.20, 0.60, and 1.96, respectively, for 6–9. Compounds 7 and 9 show much stronger quenching than 6 and 8. Compound 8 in particular is calculated to have a coplanar carbonyl group in both the ground state and excited states. Compounds 7 and 9 have twisted carbonyl groups. In contrast to the behavior of these compounds, the rigidly planar five-membered ring derivative 2 shows a quenching sensitivity that is nearly as strong as 9. The twisted carbonyl derivatives 1 and 4 show even stronger quenching. Thus, the inherent strong quenching by protic solvents will mask any additional contribution of carbonyl twisting to the deactivation process for the 1,5-Prodan series.

A second difference in behavior is the effect of solvent polarity on the quantum yield in the absence of H-bonding. For the 2,6-derivatives, the quantum yield increases with polarity, and the strongest emission is often seen in isopropanol, even with the twisted carbonyl compounds. This behavior is a result of reduced intersystem crossing to the triplet state as the excited singlet state energy is lowered. In contrast, the quantum yield decreases with increasing polarity for 1–4 as internal conversion to the ground state is enhanced by the smaller energy gap. This effect will also mask any additional contribution of carbonyl twisting to the overall deactivation.

Finally, the quantum yields are affected by the size of the ring in aprotic solvents. The larger rings show weaker emission for the same solvent. The acyclic compound 1 shows emission that is as weak as the seven-membered ring 4. The behavior for the ring derivatives is attributed to a general structural flexibility and not to carbonyl twisting specifically. This effect likewise masks contributions by carbonyl twisting to quenching since carbonyl twisting and structural flexibility due to increasing ring size go hand in hand.

Despite the masking effects above, there is some evidence for enhanced quenching due to H-bonding with the twisted-carbonyl groups in the 1,5-Prodan series. The quenching factors in methanol relative to chlorobenzene for 1–4 are 150,
20, 70, and 260, respectively. The fact that the seven-membered ring is quenched much more so that even the acyclic compound might be due to this additional contribution. The computational results show that carbonyl twisting affects the vibrational coupling of the carbonyl group with the aromatic ring. The frequency of an H-bond with the carbonyl in the excited state would be closed to the first harmonic of the carbonyl frequency, so it is reasonable to consider the carbonyl vibration and its coupling with the ring as important in the deactivation process. Deactivation can be made more efficient if the energy of the excited state can be dispersed over a greater number of vibrational modes. Hence, the coupling with the naphthalene ring may provide an explanation for the strong quenching of the 1,5-Prodan derivatives. The relevance, if any, of the progression to lower wavenumbers with increasing ring size for the main carbonyl vibration to the deactivation process remains speculative at this point.

### CONCLUSIONS

1,5-Prodan and the five-, six-, and seven-membered ring derivatives 1–4 are strongly fluorescent in moderately nonpolar, aprotic solvents. Fluorescence quantum yields decrease as the solvent polarity increases in a manner that depends on the ring size but not necessarily on carbonyl twisting. The fluorescence is strongly quenched in protic solvents. The magnitude of the quenching depends on the H-bond-donating ability of the solvent. The quenching shows some evidence for enhancement due to carbonyl twisting. However, this effect is small relative to the strong quenching by protic solvents. Further, it is obscured by the ring size-dependent deactivation caused by the energy-lowering effect of higher solvent polarity. Calculations show strong vibrational coupling between the carbonyl group and the naphthalene ring in the first excited state. The coupling shows a dependence on the carbonyl-twisting angle.

### EXPERIMENTAL SECTION

**General Information.** NMR spectra were obtained with an Agilent DD2-400 spectrometer. IR spectra were taken on a Shimadzu IRTracer-100. High-resolution ESI-MS was acquired with a Bruker Apex-Qe instrument. All solvents were spectrophotometric grade. Reagents were obtained from Acros Organics or Sigma-Aldrich. DMAC was freshly distilled with a Bruker Apex-Qe instrument. All solvents were dried under vacuum before use. Absorption and fluorescence data were collected using a fiber optic system with an Ocean Optics Maya CCD detector using a miniature deuterium/tungsten lamp and a 366 or 405 nm LED light source, respectively. Solution cells were thermostated at 23 °C. The emission intensity data was subjected to the following treatment: (1) electronic noise was subtracted, (2) the wavelength values were converted to wavenumbers, (3) the corresponding net intensity values were multiplied by \( \lambda^2/\alpha^2 \) to account for the effect of the abscissa-scale transformation, and (4) the resulting intensity values were divided by the spectral response of the Hamamatsu S10420 CCD. Electronic structure calculations were conducted using Gaussian 16. Ground-state geometries were optimized using the DFT B3LYP method employing the 6-31G+(2d,p) basis set. Relaxed, redundant coordinate (dihedral angle) scans were conducted using the 6-31G+(2d,p) basis set. Relaxed, redundant coordinate (dihedral angle) scans on the excited states were conducted using the 6-31G+(d) basis set. All calculations used the IEPPCM solvent model for acetonitrile. Zinc was activated by washing twice successively with 1.2 M HCl, EtOH, and Et2O and drying in vacuo. The organozinc reagent, 5-ethoxy-5-oxopentanoate, was freshly prepared from ethyl 5-bromopentanoate. Activated Zn (2.1 g) was covered with DMAC (15 mL) under Ar and treated with \( \text{I}_2 \) (0.39 g). After the red color was consumed, ethyl 5-bromopentanoate (4.5 g) was added, and the mixture was heated to 70 °C overnight. Titration with \( \text{I}_2 \) indicated that the organozinc concentration was 0.8 M. The reagent was dispensed through a 0.2 μL syringe filter. The preparation of 5 is described in the Supporting Information.

**6-(Dimethylamino)-2,3-dihydro-1H-cyclopenta[a]naphtalen-1-one (2).** 6-Bromo-N,N-dimethylnaphthalen-1-amine (5, 1.57 g, 6.28 mmol) was dissolved in DMAC (20 mL) under nitrogen. Bis(triphenylphosphine)nickel chloride (0.40 g, 0.61 mmol) was added, and the mixture was stirred for 15 min. A solution of 0.5 M 4-ethoxy-4-oxopropylzinc bromide (12 mL, 6 mmol) was added dropwise, and the reaction was stirred overnight. The next day, bis(triphenylphosphine)nickel chloride (0.26 g, 0.10 mmol) was added, and the reaction was stirred for 10 min. A solution of 0.5 M 4-ethoxy-4-oxopropylzine bromide (6 mL, 3 mmol) was added dropwise, and the reaction was stirred for an additional 6 h. The reaction was quenched with water (300 mL) and stirred for an hour. The organic product was salted out with NaCl (60 g) and collected by suction filtration. The solid was dried under vacuum (0.1 Torr) overnight then covered with phosphoric acid (4 mL). The slurry was heated to 110 °C for 2 h under nitrogen. The reaction was allowed to cool, covered with ice-water, and stirred overnight. The solid/liquid mixture was extracted with 33% ethyl acetate in hexanes (150 mL). The organic phase was washed with water (100 mL) and 5% NaHCO3 (100 mL), dried over CaCl2, filtered, and concentrated in vacuo. The crude product was purified by column chromatography with hexanes/EtOAc (0 → 10%) giving 2 (70 mg, 0.31 mmol, 5% over 2 steps). H NMR (CDCl3, δ): 8.87 (d, J = 8.3 Hz, 1 H), 8.50 (d, J = 8.7 Hz, 1 H), 7.57 (dd, J = 8.3, 7.7 Hz, 1 H), 7.51 (d, J = 8.7 Hz, 1 H), 7.16 (d, J = 7.7 Hz, 1 H), 3.20 (m, 2 H), 2.89 (s, 6 H), 2.79 (m, 2H); 13C NMR (CDCl3, δ): 207.48, 158.25, 151.31, 132.03, 131.26, 131.01, 129.09, 127.93, 123.0, 118.64, 115.04, 45.49, 36.99, 25.92; HRMS (ESI): [M + Na]+ calcd for C14H13N2O, 248.10485; found, 248.10434.

**8-(Dimethylamino)-2,3-dihydrophenanthrene-4(1H)-one (3).** This was prepared as above from 5 (1.17 g, 4.68 mmol) and 4-ethoxy-4-oxopropylzine bromide giving 3 and some (~15%) uncyclized ester after heating with phosphoric acid and column chromatography. The uncyclized ester was removed by saponification (50 mL of EtOH, 10 mL of H2O, and 5 g of KOH, reflux 7 h), concentration, extraction (15% EtOAc/hexanes, 125 mL), and washing (1 M NaOH, twice, 100 mL of ea; ice-cold H2O, twice, 100 mL of ea). Drying the organic layer over CaCl2, filtration, and concentration in vacuo gave 3 (0.33 g, 1.38 mmol, 29%, two steps, and saponification). H NMR (CDCl3, δ): 9.04 (d, J = 8.8 Hz, 1 H), 8.42 (d, J = 8.7 Hz, 1 H), 7.53 (dd, J = 8.8, 7.5 Hz, 1 H), 7.32 (d, J = 8.7 Hz, 1 H), 7.11 (d, J = 7.5 Hz, 1H), 3.11 (t, J = 6.3 Hz, 2H), 2.86 (s, 6H), 2.78 (t, J = 6.6 Hz, 2H), 2.19 (dd, J = 6.6, 6.3 Hz, 2H); 13C NMR (CDCl3, δ): 200.45, 151.14, 146.44, 132.82, 130.20, 128.72, 128.31, 127.74, 126.02, 14071

DOI: 10.1021/acsomega.9b01905
ACS Omega 2019, 4, 14067−14073
121.38, 114.30, 45.54, 41.16, 31.49, 23.03; HRMS (ESI): [M + Na]+ calcd for C_{17}H_{19}NONa+, 276.13588; found, 276.13562.

4-(Dimethylamino)-7,8,9,10-tetrahydro-11H-cyclohepta[α]naphthalen-11-one (4). The Negishi coupling was performed as above from 5 (0.76 g, 3.0 mmol) and 5-ethoxy-5-oxopentylzinc bromide (the second addition was not needed). The crude ester coupling product was taken up in CH₂Cl₂ (100 mL), filtered through Celite, and concentrated in vacuo. The solid (~0.43 g) was dissolved in a solution of KOH (10.0 g, 18 mmol) in EtOH (18 mL), and the mixture was heated to reflux for 4 h. The EtOH was removed in vacuo, and the residue was diluted in water (100 mL). The aqueous phase was washed three times with CH₂Cl₂ (25 mL of ea). The aqueous phase was acidified with concd aq HCl (10 mL) and then extracted three times with CH₂Cl₂ (25 mL of ea). The combined organic phases were dried over CaCl₂ filtered, and concentrated in vacuo giving the crude acid (~0.37 g). The acid was dissolved in CH₂Cl₂ (20 mL). A small amount of DMF (seven drops) was added, followed by oxalyl chloride (0.39 g, 3.1 mmol). The reaction was stirred for 1.5 h. Another portion of oxalyl chloride (0.20 g, 1.6 mmol) was added, and the reaction was stirred for 30 min. A third portion of oxalyl chloride (0.20 g, 1.6 mmol) was added but did not produce bubbles. After stirring for 5 min, the solvents were removed in vacuo, and the residue was dried in vacuo for 3 h to remove excess oxalyl chloride. The dried residue was dissolved in CH₂Cl₂ (25 mL). Aluminum chloride (0.52 g, 3.9 mmol) was added at room temperature, and the mixture was heated to reflux for 2 h. After the reaction was cooled, it was quenched with aq NaHCO₃. The mixture was poured into 15% aq NaCl (150 mL) and extracted three times with CH₂Cl₂ (50 mL of ea). The organic phases were combined, dried over CaCl₂, filtered, and concentrated in vacuo. The crude product was purified by column chromatography with hexanes/ EtOAc (0 → 10%) giving 4 (0.077 g, 0.33 mmol, 11% over four steps). ¹H NMR (CDCl₃, δ): 8.28 (d, J = 8.6 Hz, 1 H), 7.68 (d, J = 8.6 Hz, 1 H), 7.39 (dd, J = 8.6, 7.5 Hz, 1 H), 7.26 (d, J = 8.6 Hz, 1 H), 7.05 (d, J = 7.5 Hz, 1 H), 2.94 (m, 2H), 2.86 (s, 6H), 2.74 (m, 2H), 1.84 (m, J = 4H); ¹³C NMR (CDCl₃, δ): 210.74, 151.03, 136.65, 136.14, 130.88, 128.05, 127.19, 126.95, 126.49, 119.51, 113.72, 42.44, 32.58, 24.97, 22.46. HRMS (ESI): [M + Na]+ calcd for C₁₇H₁₉NONa, 276.13588; found, 276.13562.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was performed in part using facilities at William & Mary, which were provided by contributions from the National Science Foundation, the Commonwealth of Virginia Equipment Trust Fund, and the Office of Naval Research.

**REFERENCES**

(1) Weber, G.; Farris, F. J. Synthesis and spectral properties of a hydrophobic fluorescent probe: 6-propionyl-2-(dimethylamino) naphthalene. Biochemistry 1979, 18, 3075–3078.

(2) Catalan, J.; Perez, P.; Laynez, J.; Blanco, F. G. Analysis of the solvent effect on the photophysics properties of 6-propionyl-2-(dimethylamino) naphthalene (PRODAN). J. Fluoresc. 1991, 1, 215–223.

(3) Kawski, A. Ground-and Excited-State Dipole Moments of 6-Propionyl-2-(dimethylamino) naphthalene Determined from Solvatochromic Shifts. Z. Naturforsch., A 1999, 54, 379–381.

(4) Samanta, A.; Fessenden, R. W. excited state dipole moment of PRODAN as determined from transient photo-electric loss measurements. J. Phys. Chem. A 2000, 104, 8972–8975.

(5) Yequi-Supilcy, C. C.; Coutinho, K.; Lamy, M. T. New insights on the fluorescent emission spectra of Prodan and Laurdan. J. Fluoresc. 2015, 25, 621–629.

(6) Everett, R. K.; Nguyen, H. A. A.; Abel, C. J. Does PRODAN Possess an O-TICT Excited State? Synthesis and Properties of Two Constrained Derivatives. J. Phys. Chem. A 2010, 114, 4946–4950.

(7) Green, A. M.; Naughton, H. F.; Nealy, Z. B.; Pike, R. D.; Abel, C. J. Carbonyl-twisted 6-acyl-2-dialkylaminonaphthalenes as solvent aciddiy. J. Org. Chem. 2012, 78, 1784–1789.

(8) Benedetti, E.; Kocsis, L. S.; Brummond, K. M. Synthesis and photophysical properties of a series of cyclopenta[b] naphthalovolframocromic fluorophores. J. Am. Chem. Soc. 2012, 134, 12418–12421.

(9) Brummond, K. M.; Kocsis, L. S. Intramolecular Didehydro-Diels–Alder Reaction and Its Impact on the Structure–Function Properties of Environmentally Sensitive Fluorophores. Acc. Chem. Res. 2015, 48, 2320–2329.

(10) Jockusch, S.; Zheng, Q.; He, G. S.; Pudavar, H. E.; Yee, D. J.; Balsanek, V.; Halim, M.; Sames, D.; Prasad, P. N.; Turro, N. J. Two-photon excitation of fluorogenic probes for redox metabolism: dramatic enhancement of optical contrast ratio by two-photon excitation. J. Phys. Chem. C 2007, 111, 8872–8877.

(11) Chen, T.; Lee, S. W.; Abel, C. J. 1, 5-Prodan Emits from a Planar Intramolecular Charge-Transfer Excited State. ACS Omega 2018, 3, 4816–4823.

(12) Reichardt, C.; Welton, T. Solvents and Solvent Effects in Organic Chemistry; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2011.

(13) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. The solvatochromic comparison method. 6. The π* scale of solvent polarities. J. Am. Chem. Soc. 1977, 99, 6027–6038.

(14) Catalan, J. Toward a Generalized Treatment of the Solvent Effect Based on Four Empirical Scales: Dipolarity (Sdp), Polarizability (Sp), Acidity (Sa), and Basicity (Sb) of the Medium. J. Phys. Chem. B 2009, 113, 5951–5960.

(15) Catalan, J.; Diaz, C. A Generalized Solvent Acidity Scale: The Solvatochromism of o-tert-Butylstilbazolium Betaine Dye and Its Homomorph ϕ-o-Di-tert-butylstilbazolium Betaine Dye. Liebigs Ann. 1997, 1941–1949.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.

**ASSOCIATED CONTENT**

2 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01905.

Experimental procedures for the preparation of compound 5; emission spectra of 1–4 in various solvents; NMR and IR spectra of 2–4(PDF)

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: cabel@wm.edu.

**ORCID**

Christopher J. Abelt: 0000-0002-0123-8390

**Author Contributions**

The manuscript was written through contributions of all authors.
Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J.

Gaussian 16, Version 1.1, Gaussian, Inc.: Wallingford, CT, 2016.

(17) Alty, I. G.; Cheek, D. W.; Chen, T.; Smith, D. B.; Walhout, E. Q.; Abelt, C. J. Intramolecular Hydrogen-Bonding Effects on the Fluorescence of PRODAN Derivatives. J. Phys. Chem. A 2016, 120, 3518–3523.

(18) Lakowicz, J. R. Principles of Fluorescence Spectroscopy; Kluwer Academic/Plenum Publishers: New York, 1999, Vol. 2.