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Photophysical Characterization of Benzylidene Malononitriles as Probes of Solvent Friction

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Steady-state absorption and emission and femtosecond time-resolved emission spectroscopy of two benzylidene malononitriles, 2-[4-(dimethylamino)benzylidene]malononitrile (DMN) and julolidinemalononitrile (JDMN), are reported in a variety of room-temperature solvents. Solvatochromic shifts of these molecules are consistent with dielectric continuum descriptions and an S_1 – S_0 dipole moment change of 8.5 D. Time-resolved spectra show modest dynamic Stokes shifts of $\sim 1000\text{ cm}^{-1}$ occurring independently of fluorescence decay, which takes place in 0.5–5 ps in most room-temperature solvents. Absorption transition moments and fluorescence decay times are used to determine radiative rate constants: $k_{\text{rad}} = 0.32 \pm 0.02\text{ ns}^{-1}$ in DMN and $0.28 \pm 0.02\text{ ns}^{-1}$ in JDMN, assumed to be independent of solvent. Quantum yield data together with these radiative rates provide the reaction rate constants k_{rxn} associated with the internal conversion process of these molecules in 33 representative solvents at 298 K and in several solvents as functions of temperature. Reaction rates of JDMN are systematically lower than those of DMN by a factor of 2.0. Values of k_{rxn} in series of homologous solvents or in a single solvent at different temperatures are correlated to solvent viscosity η and temperature T in the manner $k_{\text{rxn}}/T \propto \eta^{-p}$ with exponents $0.2 \leq p \leq 0.8$. Solvent polarity appears to influence these reactions such that for a given viscosity reaction in high polarity solvents is significantly slower than in nonpolar solvents. However, this conclusion is predicated on the assumption that reactive friction is identical in solvents of the same viscosity, which is unlikely to be quantitatively correct. The observed reaction rates and their solvent dependence are discussed in terms of isomerization about the C=C bond occurring on a shelf-like potential.

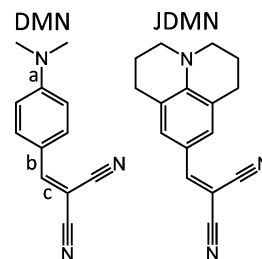
1. Introduction

Benzylidene malononitriles such as DMN and JDMN (Scheme 1) have long been used as probes of environmental fluidity and more recently as prototypical “push–pull” chromophores possessing large hyperpolarizabilities. The latter features can be qualitatively understood in terms of the essentially planar¹ S_0 and S_1 states being composed of differently weighted mixtures of the neutral and zwitterionic forms shown in Scheme 2. Electro-optic absorption measurements in dioxane solution² indicate ground state dipole moments of 8.7 D (DMN) and 9.6 D (JDMN), which increase to 17.5 D and 18.0 D, respectively, in S_1 . These large S_0 dipole moments, as well as measured bond lengths,³ indicate that significant zwitterionic character is already present in the ground electronic state. The 10 D change in dipole moment between the S_1 and S_0 states of these molecules indicates greatly increased zwitterionic character in S_1 and highlights the charge-shift nature of the $S_0 \leftrightarrow S_1$ transition, the basis for their large hyperpolarizabilities.

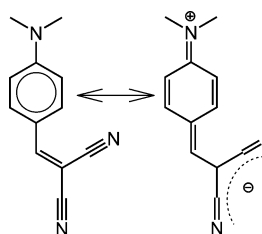
Recent studies of these chromophores have mostly centered around the work of Kelley and co-workers,^{4,5} who measured solvent-dependent resonance Raman excitation profiles of JDMN and characterized the vibronic structure of its $S_0 \rightarrow S_1$ absorption in relation to 2-state models often used in nonlinear optical analyses. A number of subsequent computational studies used semiempirical⁶ or density functional^{7–9} methods and continuum solvent models to explain and benchmark against these or related¹⁰ experimental results.

The present paper concerns instead the original focus on these compounds: their use as fluorescence indicators. Both DMN and JDMN are weakly fluorescent molecules in most room-temperature solvents, but their fluorescence quantum yields increase substantially in highly viscous media. Seminal work on the fluorescence properties of these molecules was reported by Loutfy and Law in a series of papers in the early 1980s.^{11–15} These authors characterized basic electrochemical¹¹ and photophysical properties^{11,14} of DMN, JDMN, and a related dye^{16,17} and demonstrated the sensitivity of their fluorescence yields to environmental fluidity in conventional liquid solvents.^{11,14,16}

SCHEME 1



SCHEME 2



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micellar solutions¹⁷ and polymer matrices.^{12,13} Loutfy and Law compared these molecules to *p*-dimethylaminobenzonitrile and suggested by analogy that their rapid deactivation in solution results from a twisted intramolecular charge transfer (TICT)¹⁸ process involving single-bond torsional motions about bonds *b* and possibly *a* (Scheme 1).¹¹ Despite the large solvatochromic shifts they observed¹⁴ Loutfy and Law concluded that this deactivation was insensitive to solvent polarity. Estimation of radiative rates from absorption data lead to the conclusion that internal conversion in both molecules occurs within a few picoseconds in most room-temperature solvents. In more viscous solvents at low temperatures and in polymer environments they found emission quantum yields to be exponentially related to free volumes. They therefore advocated the use of such "molecular rotors" as probes of polymer free volumes, which could be used, for example, to continuously monitor polymerization progress.^{13,15}

Roughly a decade later Torkelson and co-workers adopted this approach and showed that a variety of more complex relaxation phenomena related to aging and plasticization in polymers could also be monitored using these probes.^{19–21} In a particularly interesting study, Hooker and Torkelson used second harmonic generation (SHG) and relative fluorescence intensities to measure the overall rotation and the internal conversion of JDMN and a covalently linked relative, and reported dramatic differences between these two types of motions.²² Whereas the overall rotation of the probes measured by SHG closely tracked the viscosity-dependent α relaxation process, the relative fluorescence intensity was found to be largely decoupled from the α relaxation, changing by a factor of ~ 3 over the same temperature range that rotation times changed by $\sim 5 \times 10^6$! Thus, at least in polymer environments, the fluorescence yields apparently report on aspects of the fluidity or available space in their local environments which are distinct from viscosity or large-amplitude rotational motion.

Also in the early 1990s, Dreger, Drickamer and co-workers^{23–26} measured fluorescence yields of DMN,^{23,26} JDMN,²⁴ and a related dye²⁵ as functions of pressure in several common polymers. In the case of JDMN, fluorescence intensities were observed to increase exponentially with pressure up to about 20 kbar, implying a single deactivation process having an activation volume $\Delta V^* \cong 5 \text{ cm}^3 \text{ mol}^{-1}$ (9 \AA^3) in all four polymers examined.²⁴ In contrast, the fluorescence yields of DMN were found to increase as biexponential functions of pressure in this same collection of polymers, implying the presence of two distinct processes having activation volumes of ~ 16 and $\sim 3 \text{ cm}^3 \text{ mol}^{-1}$ (26 and 5 \AA^3).^{23,26} (For reference the van der Waals volumes of the dimethylamino group, the dimethylaniline, and malononitrile $\text{CH}_2(\text{CN})_2$ are 53, 128, and 66 \AA^3 , respectively.) These observations were interpreted to mean that fluorescence deactivation in JDMN involved solely twisting about bond *b* (Scheme 1) but that both bonds *a* (larger ΔV^*) and *b* (smaller ΔV^*) are involved in the case of DMN.²⁶

A few more studies of JDMN and closely related molecules in polymers have been published more recently by the Drickamer group^{27,28} and others.^{29–31} Most relevant here is the very recent work of Jee et al. who measured time-resolved decays of JDMN in 10 different polymers at room temperature.³¹ These authors observed nonexponential emission decays in all polymers studied, and deduced internal conversion rates from average emission lifetimes. Contrary to what might have been expected based on free-volume ideas, Jee et al. found no correlation between the measured rates and the average hole sizes of the polymers determined using positron annihilation

spectroscopy. Instead they observed an excellent correlation between the rates and the Young's moduli of the polymers.

Benzylidene malononitriles have also been used as fluorescent probes in biological contexts. Sporadic reports beginning in the late 1980s^{32–35} examined the utility of JDMN for purposes such as measuring the microviscosity of lipid bilayers³² and tubulin assembly,³³ and a similar molecule CCVJ in which one of the cyano groups was replaced with a carboxylic acid, was explored for study of antigen–antibody interactions in solution.³⁵ Over the past decade, Haidekker and Theodorakis and their co-workers have actively pursued the use of molecules such as JDMN, CCVJ, and derivatives for measuring viscosity and flow in a variety of other situations.^{36–41} Some applications include measurement of the enhanced fluidity of endothelial cell membranes under shear stress,⁴² and measurement of the viscosity of blood plasma.⁴⁰ These authors ultimately hope to be able to image the fluidity of various parts of a cell in real time using such rotor probes.⁴¹

In contrast to this activity in polymer and biological applications, relatively few studies since the initial work of Loutfy and Law have focused on the fluorescence of benzylidene malononitriles in liquid solutions.^{39,43–48} An exception has been several recent studies seeking to characterize the fluidity of room-temperature ionic liquids.^{49–52} Some interesting results emerging from the latter studies include observation of dynamic heterogeneity through the excitation wavelength dependence of fluorescence yields of DMN and JDMN⁵¹ and indications of possible changes in liquid structure with temperature in several ionic liquids.⁵² But what is lacking are studies of the fluorescence of these molecules in more conventional solvents of moderate to low viscosity. The likely reasons are the low fluorescence quantum yields and short lifetimes of DMN and JDMN in most room-temperature solvents. For these same reasons, there has been virtually no time-resolved emission data on these molecules reported to date. The one exception is an early study by Safarzadeh-Amiri⁴⁴ who used time-correlated single photon counting to measure fluorescence decays of DMN and JDMN in the high-viscosity solvents glycerol and triacetin at reduced temperatures.⁴³ Safarzadeh-Amiri observed multiexponential decays with times in the range of 10s and 100s of picoseconds. Based on our own observations in ionic liquids, it is likely that much of the dynamics was missed with the ~ 300 ps resolution available to those experiments. Safarzadeh-Amiri also noted that the temporal decays varied somewhat with emission wavelength, a feature he attributed to time-dependent solvation, consistent with results to be reported here.

In many of the applications described above, it is the fact that the nonradiative decay of benzylidene malononitriles is sensitive to the fluidity of the environment rather than the mechanism of nonradiative decay that is important. Perhaps for this reason there is little clarity in the literature concerning the deactivation mechanism. Most workers^{27,33,35,36,50,52} have simply adopted the view originally forwarded by Loutfy and Law¹¹ that deactivation involves a TICT process whereby a 90° rotation about single bonds *b* and possibly *a* (Scheme 1) leads to a nonemissive charge transfer state. Some workers^{31,44} have preferred the alternative view that the mechanism involves internal conversion via isomerization about double bond *c*, similar to the S_1 isomerization of stilbenes⁵³ and styrenes,⁵⁴ while others acknowledged both of these possibilities.^{22,45–47} Although some studies of constrained compounds were performed to provide more insight into mechanism,^{45,46} no definitive conclusions could be drawn from this work.

Two recent reports have used electronic structure calculations to help clarify the situation. In a wide-ranging study of JDMN, Allen and co-workers performed B3LYP/6-31G(d) level calculations of the ground state and CIS/6-31G(d) calculations of the S_1 state in the gas phase.⁴⁸ These authors reported potential energy scans of the S_0 and S_1 surfaces for rotation about both bonds b and c . They found twisting about bond b to be ~ 70 kJ/mol uphill in energy in both the S_0 and S_1 states, whereas twisting bond c , although highly unfavorable in S_0 , became a nearly barrierless process in S_1 leading to a minimum at 90° . These results clearly favor the isomerization mechanism over the TICT mechanism in JDMN and are in keeping with the enhanced zwitterionic character in S_1 . The same basic conclusion was reached in a more extensive study by our group¹ in which a variety of electronic structure methods were used to examine both DMN and JDMN. Exploration of the gas-phase excited state potential energy surface of DMN using the RI-CC2/def2-TZVP model chemistry revealed the presence of a shallow (6 kJ/mol) local minimum at a geometry in which the dimethylamino group is perpendicular to the benzene ring. These calculations predicted a 4 D increase in the dipole moment of this moderately emissive (oscillator strength 0.11) a -TICT state relative to the Franck–Condon state. But a variety of methods lead to the conclusion that twisting about bond b is unfavorable in S_1 even in the presence of polar solvents. SA2-CAS(12,11)/6-31G(d) calculations showed that the global minimum on the S_1 surface involves double bond isomerization and that twisting this bond (c) to 90° leads to a conical intersection with the S_0 surface. The S_1 potential was predicted to be relatively flat in this coordinate between the Franck–Condon state at 0° out to angles as large as 45° or more, with the details depending on the type of calculation performed. That work also showed that using 1-dimensional representations of the *ab initio* potentials in classical simulations of DMN interacting with a bath of acetonitrile molecules could capture the essential features of the S_1 dynamics as revealed in time-resolved spectra to be reported here. Thus, at least as a first approximation one can view the internal conversion process as isomerization on a relatively flat potential energy surface. Twisting about bond b does not seem to be relevant to the reaction, but some involvement of bond a cannot be ruled out in the case of DMN.

It is our goal to use the fluorescence of DMN and JDMN to probe friction in conventional solvents and in more unusual media such as ionic liquids. Ultimately, we hope to be able to use semiclassical simulations of the sort just mentioned to obtain a molecular-level understanding of what features of a solvent dictate the friction felt by these prototypical reactions. The present paper, together with the computational work reported in ref 1, provide the first steps toward this goal. Here we mainly survey the absorption and emission characteristics and the S_1 reaction rates of these solutes in a variety of solvents at room temperature. After describing the experimental methods in section 2, the main results of this work are described in four parts. Section 3.A concerns the spectra and their solvent dependence. Sections 3.B and 3.C concern quantum yield data and calibration of radiative rates which are needed to enable quantum yields to be used to estimate rates of the S_1 reaction. There we present the first time-resolved emission measurements of these molecules in typical room-temperature solvents. Finally, in section 3.D we examine the S_1 reaction rates in 33 assorted solvents and attempt to correlate these rates to solvent properties.

2. Experimental Section

2-[4-(Dimethylamino)benzylidene]malononitrile (DMN) was obtained from Sigma-Aldrich and purified by recrystallization

from benzene/hexane mixtures. Julolidinemalononitrile (JDMN) was obtained from Fluka and was used as received. Most solvents were from Sigma-Aldrich and were typically spectroscopic or HPLC grade and used as received except for drying over molecular sieves in some cases. The ionic liquid dimethyl(isopropyl)propylammonium bis(trifluoromethylsulfonyl)imide [$N_{ip311}[Tf_2N]$] was prepared and purified as previously described.⁵⁵

Hitachi 3000 UV/vis and Spex Fluorolog 212 spectrometers were employed for steady-state absorption and emission measurements. Emission spectra were corrected for detector responsivity using dye calibrants.⁵⁶ Samples were prepared in 1 cm quartz cuvettes at concentrations giving S_1 peak absorbances of ~ 0.1 and 1 for emission and absorption, respectively. For determination of both extinction coefficients and quantum yields, concentrated stock solutions of DMN and JDMN (~ 0.01 M) were prepared in *p*-dioxane and diluted at least 300-fold in the solvent of interest. At this level of dilution we could discern no differences in spectral shapes or position when compared to solutions made by direct addition of solid solute to the solvent. Temperature control near room temperature was provided by circulating fluid through a sample holder block. Most measurements were performed at $25.0 \pm 0.1^\circ\text{C}$. Low-temperature measurements were performed using an Oxford model DN-1754 liquid nitrogen cryostat (± 1 K).

Fluorescence quantum yield measurements on molecules as weakly fluorescent as DMN and JDMN are challenging, and we spent considerable time trying to ensure the accuracy of our measurements. The final protocol adopted was to use coumarin 153 in four solvents as reference standards. The solvents (reference quantum yields⁵⁷) used were cyclohexane (0.89), 1-chlorobutane (0.80), tetrahydrofuran (0.76), and methanol (0.42). For each sample solvent, three quantum yield measurements were made on samples having absorbances of approximately 0.05, 0.1, and 0.2 at the absorption peak. Excitation was between 395–410 nm for DMN and 412–435 nm for JDMN. For each DMN or JDMN solution two C153 reference solutions were chosen in order to have a close match for sample excitation and good overlap with the emission range of the target sample. C153 solutions were degassed by bubbling with N_2 , but DMN and JDMN solutions were not. Quantum yields φ_f of the sample (“S”) were determined relative to the two reference solutions (“R_i”) using

$$\varphi_f(S) = \frac{1}{2} \{F(R_1) + F(R_2)\} \frac{n_D^2(S)I_{em}(S)}{1 - 10^{-A(S)}} \quad (1a)$$

where

$$F(R_i) = \frac{1 - 10^{-A(R_i)}}{n_D^2(R_i)I_{em}(R_i)} \varphi_f(R_i) \quad (1b)$$

and where I_{em} is the integrated intensity of the emission spectrum, A the absorbance at the wavelength of excitation, and n_D the refractive index of the solvent. In most cases the factors $F(R_i)$ agreed to better than 10% as did the quantum yields determined using the three sample concentrations. Solvent fluorescence and Raman background levels were typically smaller than the sample fluorescence, but in some cases these unwanted signals were comparable in magnitude to the desired emission intensities. The uncertainties reported for the quantum yields reflect these variations.

As discussed later (see Table 2), the quantum yields determined here differ systematically from literature values from some laboratories and the discrepancy is as much as a factor of 3 in some cases. We explored one potential source of this discrepancy, polarization bias in the detection of emission. Fluorescence spectra and quantum yield measurements in liquid solution are typically run without intentionally polarizing either the excitation or emission. Nevertheless, in a 90° format, emission immediately after excitation is preferentially vertically polarized and only becomes unpolarized after fluorophore reorientation. Because our quantum yield standard C153 is long-lived but DMN and JDMN are short-lived relative to their rotation times, we thought that this difference in polarization together with the polarization bias of the emission monochromator might lead to erroneous quantum yield values. At least for the spectrometer used here, quantum yield measurements employing excitation and emission polarizers and magic angle detection produced results that were within uncertainties of those obtained from unpolarized experiments. Given the much lower intensities afforded in the polarized experiments, all results reported here are from unpolarized experiments.

Two instruments were used for time-resolved emission measurements. The first of these is a Kerr-gated emission (KGE) instrument described in detail previously.⁵⁸ The KGE system is based on a 250 kHz amplified Ti:sapphire laser system (Coherent RegA). Doubled light at 387 nm was used for exciting the sample, which was contained in a 1 mm thick quartz flow cell. Fundamental light was used for gating the emission in a 1 mm benzene cell which served as the Kerr medium. The instrumental response of this system is 350–450 fs as measured using Raman signals from neat solvents. To partially remove the effects of instrumental broadening, time-resolved spectra were corrected for temporal dispersion and fit using iterative reconvolution algorithms as described in ref 58. The second instrument was a fluorescence upconversion system based on a cavity dumped Ti:sapphire laser (Coherent Verdi V5/Mira 900F/APE pulse switch). The laser was dumped at a repetition rate of 2 MHz to provide 100 mW of fundamental light in pulses of ~150 fs duration. The output was doubled in a 0.2 mm β -barium borate (BBO) crystal with efficiency of about 20% and used as excitation light, which was at 400 nm for DMN and 415–430 nm for JDMN experiments. The excitation light was separated from the fundamental by a dichroic mirror, and the remaining fundamental light was passed through a computer-controlled optical delay and used for gating the emission in a 0.4 mm BBO crystal. The sample was contained in a flow cell of 0.5 mm path length and fluorescence collected with an elliptical reflector. The collection optics and electronics are essentially those previously described in ref 59. Decay data were fit to a sum-of-exponentials form via an iterative reconvolution scheme using the cross correlation between the gate and excitation pulses as an instrumental response function (IRF). The duration of the IRF typically was between 200 and 250 fs (fwhm). In both time-resolved experiments the sample was maintained at room temperature, 21 ± 1 °C.

3. Results and Discussion

A. Steady-State Spectra and Solvatochromism. Representative spectra of DMN and JDMN in *n*-hexane and dimethyl sulfoxide (DMSO) are shown in Figure 1. These spectra appear to result from a single well-isolated $S_0 \leftrightarrow S_1$ transition, a viewpoint supported by electronic structure calculations.¹ The general features of these spectra and their dependence upon solvent is similar for the two solutes. In nonpolar solvents like

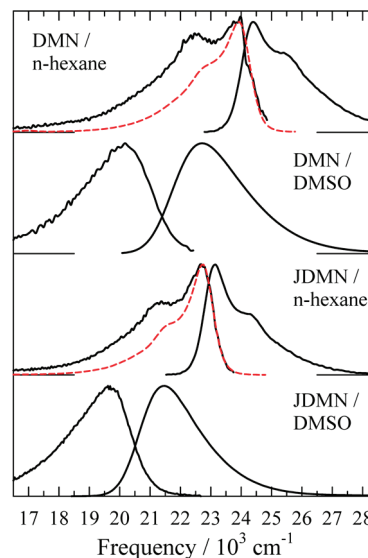


Figure 1. Representative absorption and emission spectra (solid curves) of DMN and JDMN in *n*-hexane and dimethyl sulfoxide (DMSO). The dashed lines in the *n*-hexane data are emission spectra $F_{\text{est}}(\nu)$ estimated by inverting the absorption spectra $A(\nu)$ according to $F_{\text{est}}(\nu) = \nu^2 A(2\nu_0 - \nu)$ where ν_0 is the inversion frequency.

hexane, both solutes show clear vibronic structure, composed of a sharp origin peak and a shoulder separated by roughly 1200 cm^{-1} in absorption and 1400 cm^{-1} in emission. Resonance Raman studies of JDMN⁴ have shown this shoulder to result from a composite of several active benzene and ethylene vibrations between 1000–1600 cm^{-1} . As illustrated by the dashed lines in Figure 1, the absorption and emission spectra do not display perfect mirror symmetry. In addition to a possible difference of vibrational frequencies in absorption and emission (also noted in the Raman work⁴), there appears to be greater Franck–Condon activity in emission, which suggests some change in molecular structure, for example in the average torsional angle (τ_b) or possibly larger torsional fluctuations, in S_1 compared to S_0 . In polar solvents, the absorption spectrum is broader than in nonpolar solvents and the variation is as expected for inhomogeneous solvent broadening. The same is not true of the emission spectra. The Franck–Condon activity in the emission spectra decreases with increasing solvent polarity leading to an overall narrowing of the emission band. The same sort of behavior has been observed in 4-dimethylamino-4'-cyanostilbene⁶⁰ and other highly solvatochromic molecules,^{61,62} and it can be reasonably interpreted in terms of variable mixing of neutral and zwitterionic states (Scheme 2) as a function of solvent polarity.

In order to estimate gas-phase frequencies and excited-state dipole moments we measured the absorption and emission spectra of DMN and JDMN in a range of nonpolar and polar solvents. To interpret the observed solvatochromism we employ a polarizable point dipole dielectric continuum model described in refs 60 and 63. Within this model, the absorption ν_{abs} and emission ν_{em} frequencies in solution are related to the gas-phase frequencies (ν°) and the ground (μ_0) and excited-state dipole moments (μ_1) by

$$h\nu_{\text{abs}} = h\nu_{\text{abs}}^\circ - \frac{(\mu_1^2 - \mu_0^2)}{a^3} d_c(n^2) - \frac{2\vec{\mu}_0 \cdot (\vec{\mu}_1 - \vec{\mu}_0)}{a^3} \{d_c(\epsilon) - d_c(n^2)\} \quad (2)$$

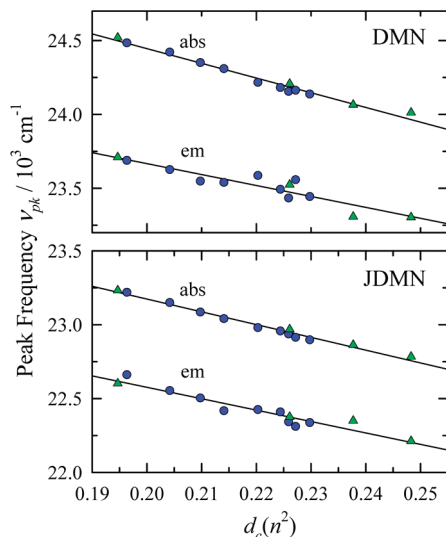


Figure 2. Peak frequencies of the absorption and emission spectra of DMN and JDMN in normal (blue circles) and other alkanes (green triangles). The lines shown here are the fits: DMN, $\nu_{\text{abs}}/10^3 \text{ cm}^{-1} = 26.43 - 9.95d_c(n^2)$, $\nu_{\text{em}}/10^3 \text{ cm}^{-1} = 25.15 - 7.40d_c(n^2)$; JDMN, $\nu_{\text{abs}}/10^3 \text{ cm}^{-1} = 24.90 - 8.64d_c(n^2)$, $\nu_{\text{em}}/10^3 \text{ cm}^{-1} = 24.12 - 7.72d_c(n^2)$.

$$h\nu_{\text{em}} = h\nu_{\text{em}}^{\circ} - \frac{(\mu_1^2 - \mu_0^2)}{a^3} d_c(n^2) - \frac{2\vec{\mu}_1 \cdot (\vec{\mu}_1 - \vec{\mu}_0)}{a^3} \{d_c(\epsilon) - d_c(n^2)\} \quad (3)$$

where a is an effective cavity radius and $d_c(x)$ is a reaction field factor involving the relative permittivity ϵ or refractive index n of the solvent. The function $d_c(x)$ is defined by

$$d_c(x) \equiv \frac{d_0(x)}{1 - 2cd_0(x)} = \frac{x - 1}{2(1 - c)x + (1 + 2c)} \quad (4)$$

Equations 1–3 allow for a (state independent) solute polarizability α , written in terms of the parameter $c = \alpha/a^3$, which can be varied between the nonpolarizable limit $c = 0$, where $d_c(x) = d_0(x) \equiv (x - 1)/(2x + 1)$, and the other common choice $c = 0.5$, wherein $d_c(x) = (x - 1)/(x + 2)$. Based on electronic structure calculations¹ we choose an intermediate value $c = 0.25$ for the present analysis, but, compared to the uncertainties introduced by use of an effective cavity size, variation of c within reasonable limits does not significantly alter the interpretation.

Figure 2 illustrates the frequencies observed in 13 alkane solvents, solvents for which only the nonpolar $d_c(n^2)$ terms in eqs 2 and 3 are relevant. Because there is little variation in spectral shape, we use the peak frequencies as the best measures of spectral position in these solvents. The correlations illustrated in Figure 2, and analogous fits using first moment frequencies, provide estimates of the gas-phase frequencies $\nu_{00} = (25.6 \pm 0.3) \times 10^3 \text{ cm}^{-1}$ for DMN and $\nu_{00} = (24.4 \pm 0.4) \times 10^3 \text{ cm}^{-1}$ for JDMN.

When polar solvents are considered, the changing shape of the spectrum renders the peak frequency an inconsistent measure of spectral position. For this reason, to analyze polar and nonpolar solvents together, we use frequency shifts measured relative to spectra in the reference solvent n -hexane. A descrip-

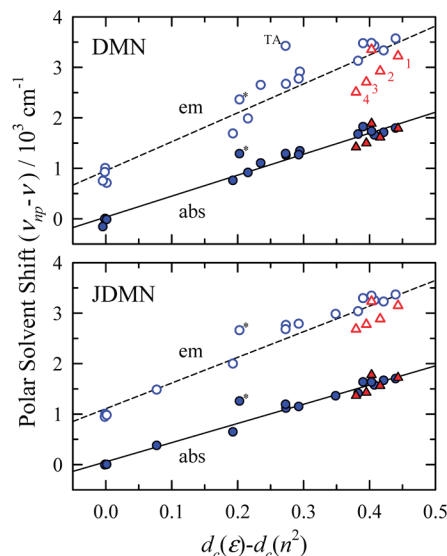


Figure 3. Absorption (filled) and emission (open symbols) shifts relative to n -hexane and corrected for the nonpolar contribution to the shift plotted versus the reaction field factor $d_c(\epsilon) - d_c(n^2)$. Blue circles denote polar aprotic solvents, and red triangles denote alcohols. Emission shifts have been increased by 1000 cm^{-1} for clarity. Solvents represented here are all of the solvents in Tables S1 and S2 except for the quadrupolar solvents benzene and p -dioxane. The asterisk marks CHCl_3 data. Labels 1–4 in the top panel denote the n -alcohols methanol to 1-butanol.

tion of the analysis method and tabulations of these data are provided in the Supporting Information (Tables S1 and S2). Figure 3 shows the “polar” portion of the solvent shifts, the portion that should depend only on the nuclear solvent polarizability represented by the $\{d_c(\epsilon) - d_c(n^2)\}$ terms in eqs 2 and 3. In order to account for variations in refractive index among solvents, the observed shifts were corrected by subtracting an amount estimated from the nonpolar solvent correlations from Figure 2. Consider first the absorption data, shown as the filled symbols in Figure 3. With the exception of CHCl_3 (*), the polar absorption shifts are well-correlated to the reaction field factor $\{d_c(\epsilon) - d_c(n^2)\}$ ($r^2 = 0.97$ – 0.98 for 21 solvents), as expected from dielectric continuum theory. It is noteworthy that alcohol solvents (triangles) do not show any distinctive behavior compared to the aprotic solvents (circles). Hydrogen bonding to the CN groups of these malononitriles, which might occur in alcohol solvents, must therefore contribute negligibly to their solvatochromism. This observation is consistent with the small changes in CN atom charges between S_0 and S_1 predicted by electronic structure calculations.¹

The polar emission shifts (open symbols) in Figure 3 are also clearly correlated to $\{d_c(\epsilon) - d_c(n^2)\}$, but there is considerably more scatter in these data, especially in the case of DMN ($r^2 = 0.87$ for DMN and 0.94 for JDMN). Although some of this difference is likely due to the larger uncertainties in measuring the weak emission of these molecules, the primary reason for the greater scatter is that the emission spectra are not all equilibrated. As will be discussed in section 3.C, the lifetimes of DMN and JDMN are near 1 ps in most room-temperature solvents, a time comparable to or shorter than solvation times.⁵⁹ Assuming that these molecules exhibit a significant solvation Stokes shift (we estimate $\sim 1000 \text{ cm}^{-1}$ in high-polarity solvents), their steady-state emission will occur at higher frequencies than would equilibrated spectra, and the extent of this departure from equilibrium depends upon the ratio of the solvation time to the fluorescence lifetime. Among common room-temperature sol-

vents, the normal alcohols are distinctive for having unusually long solvation times, which range from 5 to 60 ps in the series methanol to *n*-butanol. It is for this reason that the emission shifts in these *n*-alcohols (open triangles, labeled 1–4 in the top panel of Figure 3) depart most from the overall correlation. The larger departure of these solvents in the case of DMN compared to JDMN is also readily explained by the roughly 2-fold shorter emission lifetimes of DMN. Thus, analysis of steady-state emission shifts in the context of equilibrium solvation models such as the model leading to eq 2 is dangerous.

Finally we consider what the solvatochromic data in Figures 2 and 3 indicate about the dipole moments of these solutes. The slopes in these plots can be used to infer the change in dipole moment between the S_0 and S_1 states if the ground-state dipole moment and an estimate of the effective cavity radius are available. Several previous studies provide consistent values of the S_0 dipole moments of DMN and JDMN of $\mu_0 = 8.6 \pm 0.2$ D^{2,64–66} and 9.5 ± 0.1 D,^{2,65} respectively. Reasonable estimates of the effective cavity radii can be obtained using by increasing the spherical radii produced by the van der Waals volumes of the solutes by some amount to account for the effective size of solvent molecules. For the latter we assume a value 2.0 Å, which is intermediate between the average radius of a solvent atom (~ 1.5 Å) and a solvent molecule (~ 2.6 Å). Given van der Waals volumes⁶⁷ of 193 Å³ and 239 Å³ for these two molecules, effective cavity radii we estimate are 5.6 Å for DMN and 5.9 Å for JDMN. Although the ill-defined nature of the cavity size is always a concern for solvatochromic analysis of nonspherical molecules such as these, this choice yields radii close to what one finds from the relationship between dipole moments and electrostatic interaction energies observed in molecular dynamics simulations of DMN and JDMN in CH₃CN, which average 5.4 ± 0.3 Å and 5.6 ± 0.4 Å, respectively.⁶⁸ Thus, in the present case, we do not expect ambiguities in choice of a to greatly limit the accuracy of solvatochromic dipole moment estimates. Using these values of a , μ_0 , and $\alpha/a^3 = 0.25$, the absorption data measured in all solvents (~ 30 solvents for each solute; Supporting Information) are well represented by eq 1 for values of

$$\Delta\mu = 8.4 \text{ D (DMN) and } \Delta\mu = 8.5 \text{ D (JDMN)}$$

(We assume here that μ_1 is collinear with μ_0 , which is a good approximation according to electronic structure calculations.¹) These solvatochromic estimates are in excellent agreement with the values $\Delta\mu = 8.8$ D (DMN) and 8.4 D (JDMN) determined from electrochromic measurements in dioxane.²

B. Transition Moments and Quantum Yields. Reaction rates in DMN and JDMN near room temperature have thus far only been estimated from measurements of emission quantum yields combined with various assumptions concerning radiative rates. Although it is possible to make more direct measurements of the rates from fluorescence decays as will be discussed in the following section, quantum yield estimates still provide the most convenient method for surveying the behavior of these molecules in a wide range of solvents. For this reason, in this section we describe emission quantum yields and other steady-state data that will be used later to estimate decay/reaction rates.

Triplet formation in DMN and JDMN is not detectable,^{11,48} and, at least near room temperature, reaction rate constants k_{rxn} can be assumed equal to nonradiative decay rate constants k_{nr} . The latter are in turn related to fluorescence quantum yields φ_f and radiative rate constants k_{rad} by

$$k_{\text{rxn}} \cong k_{\text{nr}} = k_f - k_{\text{rad}} = k_{\text{rad}} \left(\frac{1}{\varphi_f} - 1 \right) \quad (5)$$

where $k_f = k_{\text{rad}} + k_{\text{nr}}$ is the total fluorescence decay rate constant. Thus, to measure reaction rates from emission quantum yields one only needs values of the radiative rate. If the assumption is made that the electronic transition moment for absorption, M_{01} , is equal to that for emission, M_{10} , the Strickler–Berg relationship^{57,69,70} can be used to estimate k_{rad} from the S_1 absorption band:

$$k_{\text{rad}}/\text{s}^{-1} = 2.88 \times 10^{-9} n^2 (\tilde{\nu}_{\text{em}}^3 / \text{cm}^{-3}) \times \int_{S_1} \frac{\varepsilon(\nu) / (M^{-1} \text{cm}^{-1})}{\nu} d\nu \quad (6)$$

ε in this expression is the molar extinction coefficient, n the solvent refractive index, and $\tilde{\nu}_{\text{em}}^3$ a characteristic frequency of the emission spectrum $F(\nu)$ defined by

$$\tilde{\nu}_{\text{em}}^3 \equiv \frac{\int F(\nu) d\nu}{\int F(\nu) \nu^{-3} d\nu} \quad (7)$$

Data on the S_1 absorption band of DMN and JDMN relevant to calculation of k_{rad} in a range of solvents are summarized in Table 1. The maximal molar extinction coefficients ε_{max} measured here are in the range $5\text{--}7 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ for both compounds. Our values are in reasonable agreement with literature values (mainly from the work of Loutfy and Law¹¹), but the DMN values are systematically higher by an average of 14% and the JDMN values lower by 5%. In addition to estimates of k_{rad} , we also list values of the absorption transition moments calculated from^{57,70}

$$M_{01}/\text{D} = 9.58 \times 10^{-2} \left(\frac{1}{n} \int_{S_1} \frac{\varepsilon(\nu) / (M^{-1} \text{cm}^{-1})}{\nu} d\nu \right)^{1/2} \quad (8)$$

To within uncertainties, both k_{rad} and M_{01} appear to be independent of solvent. Allen et al.⁴⁸ also recently reported k_{rad} of JDMN = 0.28 ns^{−1} in room-temperature methylcyclohexane using the Strickler–Berg relation, close to the values determined here in cyclohexane and *n*-hexane. We note that several authors have previously reported estimates of k_{rad} based on a variant of eq 6 introduced by Loutfy and Law,^{11,71}

$$k_{\text{rad}} \cong 2.88 \times 10^{-9} (\nu_{\text{abs}}^{\text{mx}})^2 \int \varepsilon(\nu) d\nu \quad (9)$$

where $\nu_{\text{abs}}^{\text{mx}}$ is the frequency of maximum absorption. These authors reported $k_{\text{rad}} = 0.28 \text{ ns}^{-1}$ (DMN) and 0.27 (JDMN) in ethyl acetate, and later authors^{45,46} using this same expression reported 0.29 ns^{−1} (DMN) and 0.27 ns^{−1} (JDMN) in glycerol. The fact that these values are also close to the values obtained here must be considered coincidental given the neglect of the refractive index and the distinction between absorption and emission frequencies in eq 9.

Fluorescence quantum yields of DMN and JDMN are summarized in Table 2. In these solvents of low to moderate viscosity all quantum yields are close to 10^{−3}, with the yields in JDMN being typically 2-fold larger than in DMN. Also shown

TABLE 1: Properties of the S₁ Absorption Band of DMN and JDMN in Selected Solvents^a

solvent	n_D	DMN				JDMN			
		$\langle\nu\rangle^a/10^3\text{ cm}^{-1}$	$\epsilon_{\text{max}}/10^3\text{ M}^{-1}\text{ cm}^{-1}$	M_{01}/D	$k_{\text{rad}}/\text{ns}^{-1}$	$\langle\nu\rangle^a/10^3\text{ cm}^{-1}$	$\epsilon_{\text{max}}/10^3\text{ M}^{-1}\text{ cm}^{-1}$	M_{01}/D	$k_{\text{rad}}/\text{ns}^{-1}$
<i>n</i> -hexane	1.372	25.45	71, 57	6.8(4)	0.39(5)	24.38	67, 68	6.4(3)	0.31(3)
cyclohexane	1.424	25.25	69	6.5(4)	0.38(5)	24.28	71 [72 ^d]	6.5(3)	0.34(3)
ethyl acetate	1.370	24.26	59 [51 ^b]	7.1(4)	0.34(4)	23.47	54 [59 ^b]	6.9(3)	0.28(2)
tetrahydrofuran	1.405	24.10	62 [51 ^b]	7.1(4)	0.36(4)	23.31	58 [62 ^b]	7.0(3)	0.31(3)
acetonitrile	1.341	23.88	52, 53 [49 ^b]	6.8(3)	0.26(3)	23.02	55, 63 [60, ^b 58 ^d]	7.1(3)	0.27(2)
dimethyl sulfoxide	1.477	23.29	60	7.0(4)	0.35(4)	22.60	51	6.6(3)	0.29(3)
1-butanol	1.397	23.96	51	7(1)	0.30(9)	23.12	50	7(1)	0.27(8)
methanol	1.327	23.91	55, 56 [50 ^b]	7.1(4)	0.29(3)	23.06	52, 66 [62, ^b 58 ^d]	7.0(3)	0.26(2)
<i>p</i> -dioxane	1.420	24.48	61 [50 ^c]	7.1(4)	0.39(4)	23.64	55 [55 ^c]	7(1)	0.32(9)
benzene	1.498	24.23	52 [47 ^b]	6(1)	0.34(11)	23.44	50 [63 ^b]	6.0(3)	0.30(3)

^a Measurements were made at room temperature, 21 ± 1 °C. n_D is the solvent refractive index from ref 113, $\langle\nu\rangle$ the first moment frequency, ϵ_{max} the maximum value of the molar extinction coefficient, M_{01} the transition moment (eq 8) and k_{rad} the estimated radiative rate (eq 6). Values in parentheses indicate uncertainties in the final digits. Values in square brackets are literature data. ^b Reference 11. ^c Reference 2. ^d Reference 4.

TABLE 2: Fluorescence Quantum Yields and Reaction Rates (25 °C)^a

no.	solvent	η/cP	DMN			JDMN		
			$\varphi_f/10^{-3}$	lit. $\varphi_f/10^{-3}$	$k_{\text{rxn}}/\text{ps}^{-1}$	$\varphi_f/10^{-3}$	lit. $\varphi_f/10^{-3}$	$k_{\text{rxn}}/\text{ps}^{-1}$
1	<i>n</i> -pentane	0.21	0.22(4)		1.5(3)	0.34(7)		0.8(2)
2	<i>n</i> -hexane	0.30	0.23(3)		1.4(2)	0.36(5)		0.77(13)
3	<i>n</i> -heptane	0.39	0.26(5)		1.3(3)	0.42(8)		0.7(1)
4	<i>n</i> -octane	0.51	0.25(4)		1.3(2)	0.45(7)		0.63(10)
5	<i>n</i> -decane	0.84	0.30(6)		1.1(2)	0.54(11)		0.52(11)
6	<i>n</i> -dodecane	1.37	0.32(6)		1.0(2)	0.57(11)		0.49(10)
7	<i>n</i> -tridecane	1.71	0.33(7)		1.0(2)	0.58(12)		0.48(10)
8	<i>n</i> -tetradecane	2.11	0.34(7)		0.9(2)	0.7(2)		0.39(12)
9	<i>n</i> -hexadecane	3.05	0.35(5)		0.9(2)	0.72(11)		0.39(6)
10	2-methylbutane	0.22	0.22(4)		1.5(3)	0.31(6)		0.9(2)
11	cyclohexane	0.90	0.26(4)		1.2(2)	0.47(9)		0.59(13)
12	decalin	2.42	0.39(8)		0.8(2)	0.7(2)		0.41(13)
13	squalane	28.3	0.24(5)		1.4(3)	0.7(2)		0.41(13)
21	diisopropyl ether	0.38	0.29(6)		1.1(2)	0.49(10)		0.57(12)
22	ethyl acetate	0.43	0.50(1)	0.9 ^b	0.6(1)	1.0(2)	3.0 ^b	0.28(6)
23	tetrahydrofuran	0.46	0.54(1)	1.5 ^b	0.6(1)	1.2(2)	3.3 ^b	0.24(5)
24	acetone	0.30	0.6(2)		0.6(2)	0.7(3)		0.4(2)
25	acetonitrile	0.34	0.43(9)	1.1 ^b	0.7(2)	0.44(9)	1.5 ^b	0.63(13)
26	dimethylformamide	0.80	1.1(2)		0.30(6)	0.9(4)		0.3(1)
27	dimethyl sulfoxide	1.99	1.3(3)		0.25(5)	1.5(3)		0.19(4)
28	propylene carbonate	2.53	1.6(5)		0.20(7)	1.3(5)		0.22(9)
29	HMPA	3.11	1.8(4)		0.17(4)	2.8(8)		0.10(3)
31	methanol	0.55	0.39(8)	1.0 ^b	0.8(2)	0.54(11)	2.2, ^b 0.70 ^c	0.52(11)
32	ethanol	1.08	0.54(11)		0.59(12)	0.9(2)	0.91 ^c	0.33(7)
33	1-propanol	1.94	0.60(12)		0.52(11)	1.1(2)	0.95, ^c 2.9 ^d	0.25(5)
34	1-butanol	2.57	0.50(10)		0.64(13)	1.2(2)	1.04 ^c	0.22(5)
35	1-pentanol	3.51	0.67(13)		0.48(10)	1.4(3)	1.25 ^c	0.20(4)
36	1-heptanol	5.78	0.62(12)		0.52(11)	1.7(3)	1.53 ^c	0.17(4)
37	1-nonanol	9.10	0.62(12)		0.52(11)	1.9(4)	1.56 ^c	0.15(3)
38	1-decanol	11.3	0.67(13)		0.48(10)	1.9(4)	1.58 ^c	0.15(3)
39	1,2-ethanediol	17.3	1.8(4)		0.18(4)	2.9(6)	11.1 ^d	0.10(2)
41	<i>p</i> -dioxane	1.19	0.48(10)		0.7(1)	1.1(2)		0.25(5)
42	benzene	0.60	0.39(8)	0.8 ^b	0.8(2)	1.0(2)	3.0 ^b	0.29(6)

^a η is the solvent viscosity from ref 113. φ_f is the fluorescence quantum yield and k_{rxn} the reaction rate estimated from these φ_f using eq 5 and assuming constant values of $k_{\text{rad}} = 0.32\text{ ns}^{-1}$ for DMN and 0.28 for JDMN. Values in parentheses indicate uncertainties in the final digits. HMPA = hexamethylphosphoramide. ^b Reference 11. ^c Reference 48. ^d Reference 32.

in Table 2 are all direct comparisons with literature values of φ_f presently available. Prior results stem primarily from two studies. The values reported in the seminal work of Loutfy and Law¹¹ are systematically larger than the values measured here. On average these values are roughly a factor of 2 larger in the case of DMN and a factor of 3 in JDMN. The reason for this disagreement is not known, but as discussed in the Experimental Section, accurate measurement of such low quantum yields is challenging. Much better agreement, to within estimated uncertainties, is found with the more recent JDMN quantum yields reported by Allen et al.⁴⁸

C. Time-Resolved Emission and k_{rad} Calibration. Figures 4 and 5 contain examples of time-resolved emission data. These data are of two types. In Figure 4 we show complete time-resolved emission spectra of DMN which were recorded using the Kerr-gated emission (KGE) technique.⁵⁸ These spectra have been fit with an iterative reconvolution algorithm in order to partially remove the temporal broadening caused by the 350–450 fs response of this instrument. The spectra recorded in cyclohexane show no marked obvious change in width or shape with time, only an overall decay of intensity with a time constant of 0.7 ps. In acetonitrile the intensity decay is

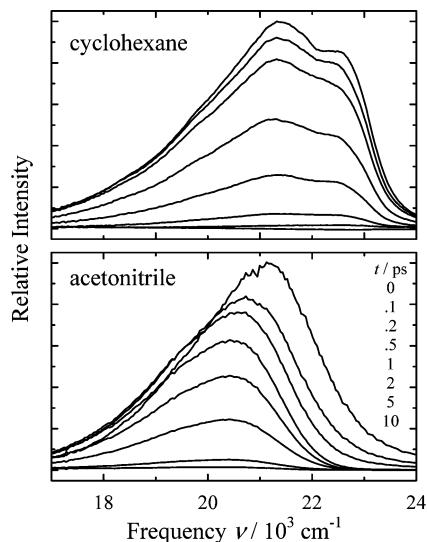


Figure 4. Time-resolved spectra of DMN recorded using the Kerr-gated emission technique. These spectra have been fit using an iterative reconvolution algorithm so as to partially remove the broadening caused by the ~ 400 fs instrument response of the KGE system. Intensity decreases with time; the same set of 8 times is plotted on both panels.

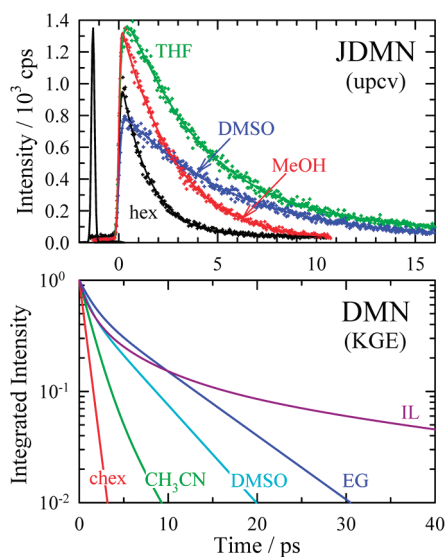


Figure 5. Representative intensity decays in several solvents. The top panel shows single-wavelength emission decays of JDMN recorded using fluorescence upconversion. Raw data (points) and single or biexponential fits (smooth curves) are shown. The spike prior to $t = 0$ is the instrument response (~ 200 fs fwhm). The bottom panel are integrated intensity decays (ν^3 -normalized) spectra of DMN obtained using the KGE technique. These decays have been fit so as to remove instrumental broadening. The solvents shown here are hex = *n*-hexane, THF = tetrahydrofuran, DMSO = dimethyl sulfoxide, MeOH = methanol, chex = cyclohexane, and EG = ethylene glycol. “IL” in the bottom panel denotes the ionic liquid solvent $[N_{ip311}][Tf_2N]$.

accompanied by a Stokes shift of the spectrum of roughly 1000 cm^{-1} . This shift occurs on the time scale expected for the solvation response in acetonitrile ($\sim 0.2\text{ ps}$)⁵⁹ which is much faster than the time constant associated with the decay of spectral intensity, 1.4 ps . We observe dynamic Stokes shifts of comparable magnitude in other highly polar solvents, and the time scales of these shifts likewise appear to match solvation times rather than intensity decay times. Such observations suggest that the modest spectral shifts observed are due to solvation of the initially formed S_1 state rather than to intramolecular changes,

although we cannot exclude contributions from the latter source, especially at longer times where the spectra are noisy.

Emission intensity decays are shown in Figure 5. In the top panel are representative decays of JDMN at single emission wavelengths collected using the fluorescence upconversion method. We cannot currently obtain KGE spectra of JDMN because its absorption lies outside of the range of the excitation source used for this experiment. For this reason we have collected emission decays at several wavelengths near the emission peak, similar to those shown in Figure 5, and used average values from these decays to determine the emission lifetimes. Although there will be some residual effect of the dynamic Stokes shift in such decay data, the times deduced in this manner provide reasonable estimates of the overall intensity decay, as evidenced by the comparisons we have made between KGE and upconversion data using the solute DMN. The bottom panel of Figure 5 shows intensity decay data for DMN obtained from KGE spectra. These decays are the integrated emission intensities of ν^3 normalized spectra obtained from iterative fits of the moments of the time-resolved spectra as described in ref 58. (The ν^3 normalization removes the effect of the dynamic Stokes shift from the decay data.⁷²) In both the upconversion data on JDMN and the KGE data on DMN, the intensity decays are often not single exponential functions of time. As illustrated in the bottom panel of Figure 5, the departure from exponentiality varies with solvent, with the most viscous solvents ethylene glycol (EG) and especially the ionic liquid $[N_{ip311}][Tf_2N]$ being the most nonexponential in nature. It seems likely that this nonexponentiality results, at least in part, from dynamic heterogeneity in solvents whose reorganization times are longer than the (average) emission lifetime.⁵¹ We will discuss this point further in section 3.D. For now we note that, in order to deduce radiative rates in cases of nonexponential decay, the average fluorescence decay times $\langle\tau_f\rangle$ should be used in the manner

$$k_{\text{rad}} = \frac{\varphi_f}{\langle\tau_f\rangle} \quad (10a)$$

where

$$\langle\tau_f\rangle = \frac{\int_0^\infty I(t) dt}{I(0)} \quad (10b)$$

and $I(t)$ is the decay profile.

Table 3 lists the average decay times measured in a variety of solvents and the radiative rates deduced from them according to eq 10a. Also listed are the transition moments calculated from these radiative rates via^{57,70}

$$M_{10}/D = 1.786 \times 10^3 \left(\frac{k_{\text{rad}}/s}{n^3 \tilde{\nu}_{\text{em}}^3/\text{cm}^{-3}} \right)^{1/2} \quad (11)$$

Figure 6 plots radiative rates estimated from quantum yields and lifetimes as well as those obtained from absorption data via the Strickler–Berg relation (eq 6). These data are plotted versus the first moment absorption or emission frequencies in order to help expose any solvent dependence. (See Figure S1 in the Supporting Information for analogous plots of transition moments.) If one makes the reasonable assumption that the transition moments should be independent of solvent, eq 11

TABLE 3: Fluorescence Decay Times^a

solvent	n_D	$\langle\tau\rangle/\text{ps}$	$\langle\nu_{\text{em}}\rangle/10^3\text{ cm}^{-1}$	$k_{\text{rad}}/\text{ns}^{-1}$	M_{10}/D
DMN					
<i>n</i> -hexane	1.372	0.69(8)	22.19	0.33(6)	6.1(6)
cyclohexane	1.424	0.7(2)	22.00	0.36(9)	6.1(8)
decalin	1.479	0.9(2)	21.87	0.43(12)	6.3(9)
squalane	1.452	0.9(2)	21.50	0.27(9)	5.3(9)
benzene	1.498	1.3(3)	20.91	0.29(8)	5.5(8)
ethyl acetate	1.370	1.6(3)	20.49	0.30(9)	6.6(9)
tetrahydrofuran	1.405	2.1(4)	20.37	0.25(7)	5.8(8)
acetonitrile	1.341	1.4(5)	19.65	0.30(12)	7(1)
dimethyl sulfoxide	1.477	3.6(7)	19.41	0.34(10)	7(1)
methanol	1.327	1.8(4)	20.12	0.22(6)	6.0(8)
1-butanol	1.397	1.9(2)	20.55	0.26(6)	5.9(7)
1,2-ethanediol	1.431	7.7(10)	19.67	0.23(6)	5.8(7)
JDMN					
<i>n</i> -hexane	1.372	1.4(2)	21.60	0.26(5)	5.6(6)
<i>n</i> -octane	1.395	2.2(8)	21.31	0.20(8)	4.9(9)
<i>n</i> -dodecane	1.420	2.1(5)	21.47	0.27(9)	5.6(9)
<i>n</i> -hexadecane	1.433	2.5(9)	21.47	0.29(11)	5.6(10)
cyclohexane	1.424	1.2(3)	21.31	0.38(12)	6.6(10)
<i>p</i> -dioxane	1.420	5.1(10)	19.89	0.22(6)	5.6(8)
ethyl acetate	1.370	3.9(8)	19.58	0.25(7)	6.4(9)
tetrahydrofuran	1.405	5.5(11)	19.58	0.21(6)	5.7(8)
acetonitrile	1.341	2.0(2)	19.58	0.22(5)	6.2(7)
dimethyl sulfoxide	1.477	4.0(8)	18.99	0.35(10)	7.2(10)
methanol	1.327	2.5(5)	19.46	0.22(6)	6.3(9)
1-butanol	1.397	5.3(10)	19.68	0.22(6)	5.9(8)

^a Measurements are at 21 ± 2 °C. n_D is the solvent refractive index from ref 113. $\langle\tau\rangle$ is the integral decay time of emission intensity measured with the KGE experiment, $\langle\nu_{\text{em}}\rangle$ is the first moment of the steady-state emission spectrum and k_{rad} and M_{10} are the radiative rate constants and the emission transition moments calculated according to eqs 10a and 11.

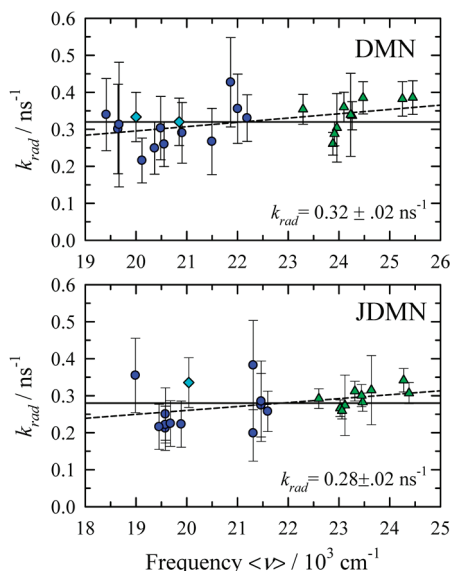


Figure 6. Estimates of radiative rate constants plotted versus first-moment absorption or emission frequencies. Triangles (green) are data from absorption measurements, circles (blue) are from the combination of time-resolved and steady-state fluorescence measurements near room temperature, and the diamonds (cyan) are similar measurements in glassy solvents near 80 K. The solid lines indicate weighted averages of all data yielding the values indicated, and the dashed lines are the linear regressions: $k_{\text{rad}} = 0.063 + 0.012\langle\nu\rangle$ (DMN) and $k_{\text{rad}} = 0.048 + 0.011\langle\nu\rangle$.

indicates $k_{\text{rad}} \propto n^3 \bar{\nu}_{\text{em}}^3$. To within the sizable scatter in these data, no clear dependence on refractive index could be found and any frequency dependence that might be present (dashed lines in Figure 6) is considerably weaker than ν^3 . Given these

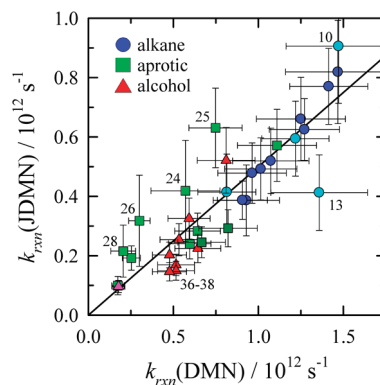


Figure 7. Comparison of DMN and JDMN reaction rates (25 °C) estimated from fluorescence quantum yields. Blue circles denote *n*-alkanes and cyan circles branched or cyclic alkanes. Red triangles denote *n*-alcohols and the pink triangle ethylene glycol. Green squares denote polar aprotic solvents (no. 21–29) and dark green squares non-dipolar solvents (no. 41–42). The numbers denote solvents as listed in Table 2. The solid line is the proportionality $k_{\text{rxn}}(\text{JDMN}) = 0.50 k_{\text{rxn}}(\text{DMN})$ ($N = 33$; $R^2 = 0.95$).

observations it seems best to assume here, as has been done in all prior work, that k_{rad} is solvent independent. Based on the above data we recommend use of the values $k_{\text{rad}} = 0.32 \pm 0.02 \text{ ns}^{-1}$ for DMN and $0.28 \pm 0.02 \text{ ns}^{-1}$ for JDMN.

D. Estimated Reaction Rates and Solvent Dependence.

Reaction rates estimated from emission quantum yields via eq 5 and adopting these constant values of k_{rad} are summarized in Table 2 and plotted in Figure 7. As already evident in the previous section, these reactions are quite rapid in room-temperature solvents: DMN rates exceed 10^{12} s^{-1} in many cases. As shown in Figure 7 there is a good correlation between the reaction rate constants of DMN and JDMN in the wide variety of solvents studied here. The solid line in this figure shows the best fit proportionality $k_{\text{rxn}}(\text{JDMN}) = (0.50 \pm 0.02) k_{\text{rxn}}(\text{DMN})$. This relationship holds to within the estimated uncertainties for most of the data, but systematic deviations are apparent in the case of the stiff linear alkane squalane (no. 13), the most polar of the aprotic solvents (no. 25–28), and the longer *n*-alcohols (no. 36–38).

In considering the parallel behavior of DMN and JDMN and the solvent dependence to be discussed next, it is helpful to review what is known about the intramolecular motions involved in these reactions. As discussed in the Introduction, electronic structure calculations indicate that internal conversion results from double bond isomerization.^{1,48} The S_1 torsional potential for twisting about the double bond in DMN is predicted to be relatively flat out to angles of 40–50° and thereafter to drop more or less steeply, depending on the model chemistry employed, to a conical intersection with S_0 at 90°. (See Figure 11.) One can therefore view the reaction rate as being determined by the time required for molecules to twist from their Franck–Condon angles near $\tau = 0$ to $\tau \sim 45^\circ$, driven by minimal intramolecular forces but under the frictional influence of the solvent molecules packed around the rotating moieties. Twisting is effected by the differential rotation of the malononitrile and benzyl portions of the molecule. Preliminary simulations of the sort described in ref 1 suggest that the greater solvent friction on the motion of the julolidine group in JDMN compared to the dimethylaniline group of DMN is primarily responsible for the 2-fold difference in reaction rates observed.

An initial appreciation for how much solvent friction affects these reactions can be obtained by considering free inertial motion. Using the moment of inertia of the malononitrile group

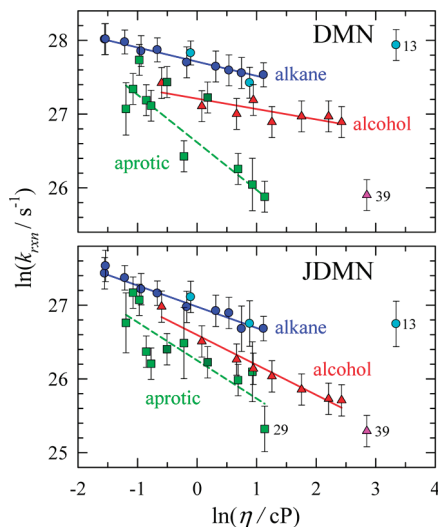


Figure 8. Reaction rates (25 °C) estimated from fluorescence quantum yields plotted versus solvent viscosity. (Symbols as in Figure 7.) The solid lines here are fits of the *n*-alkane and *n*-alcohol series data to the function $\ln(k_{\text{rxn}}) = A - p \ln(\eta)$ with the slopes p listed in Table 4. The dashed lines are similar fits to the polar aprotic data (no. 21–29).

about the double-bond axis ($166 \text{ m}_0 \text{ \AA}^2$) to gauge inertial motion, one calculates the average free rotation frequency of this torsion to be $\omega_\tau \sim 1.2 \text{ ps}^{-1}$. The time required for 45° rotation at this frequency is 0.6 ps, a time comparable to the fastest reaction time measured, 0.7 ps for DMN in *n*-pentane. Thus, if these reactions are viewed in terms of motion on a flat potential, solvents such as *n*-pentane must exert very little friction on the reaction in DMN.

With these perspectives in mind, we now consider the solvent dependence of the reaction rates. If frictional effects are of primary importance and if a hydrodynamic perspective is valid, one would expect friction on the reaction to be proportional to solvent viscosity η and, in the absence of barrier, rates to be proportional to T/η . In Figure 8 we therefore plot the observed reaction rate constants at 25 °C versus solvent viscosity. As illustrated here, reaction rates and viscosity appear to be related, at least within homologous series of solvents such as the *n*-alkanes and *n*-alcohols. Whether such a relationship also holds in a collection of unrelated solvents, for example the polar aprotic solvents, is less obvious. But even in the homologous series, the dependence of rate upon viscosity is much weaker than the inverse relationship expected from hydrodynamics. The solid lines in these logarithmic plots are fits to a power law form, $k_{\text{rxn}} \propto \eta^{-p}$, with exponents in the range $0.1 < p < 0.5$. Given such small exponents, one might question whether the correlations in Figure 8 actually indicate a significant solvent frictional effect or whether they might merely result from a secondary correlation with some other solvent property. More convincing evidence of the influence of friction is provided by temperature-dependent data of the sort shown in Figure 9. These data were obtained from quantum yield measurements and assumptions about radiative rates in the same manner as the data in Table 2.⁷³ In the glass-forming liquids 2-methyltetrahydrofuran and 1-propanol, the reaction appears to turn off at sufficiently high viscosities (low temperatures). The lines in Figure 9 indicate viscosity dependence of the form $(k_{\text{rxn}}/T) \propto \eta^{-p}$ with exponents $p = 0.7\text{--}0.8$ for both solutes in 2-methyltetrahydrofuran and $p \sim 0.4$ for DMN in 1-propanol and the ionic liquid $[\text{N}_{\text{ip}311}][\text{Tf}_2\text{N}]$.⁷⁴ These observations are consistent with a barrierless torsional reaction but again with solvent

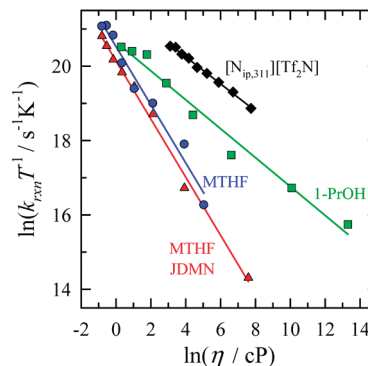


Figure 9. Reaction rates as functions of temperature in selected solvents estimated from quantum yields as described in the text. The red triangles labeled “MTHF/JDMN” denote data on JDMN, and the remaining data are for the DMN solute. The solvents are 2-methyltetrahydrofuran (MTHF), 1-propanol (1-PrOH) and the ionic liquid $[\text{N}_{\text{ip}311}][\text{Tf}_2\text{N}]$. The lines are fits to the relation $\ln(k_{\text{rxn}}/T) = A - p \ln(\eta)$. The temperature and viscosity ranges of these data and the slopes p are summarized in Table 4.

TABLE 4: Summary of Viscosity Exponents^a

solvent	<i>T</i> /K	η /cP	#	<i>p</i>	ref
DMN					
<i>n</i> -alkanes	298	0.2–3	9	0.19	this work
<i>n</i> -alcohols	298	0.6–11	8	0.14	this work
2-methyltetrahydrofuran	125–298	0.5–34	8	0.69	this work
ethyl acetate	295–349	0.3–0.4	7	1.1	14
dimethyl phthalate	298–378	2–14	9	0.43	14
1-propanol	135–298	$2-3 \times 10^5$	8	0.39	this work
glycerol	297–366	6–1040	8	0.61	14
$[\text{N}_{\text{ip}311}][\text{Tf}_2\text{N}]$	258–338	22–2300	9	0.40	this work
JDMN					
<i>n</i> -alkanes	298	0.2–3	9	0.29	this work
<i>n</i> -alcohols	298	0.6–11	8	0.41	this work
<i>n</i> -alcohols	293	0.5–11	10	0.29	48
alcohols + glycerol	RT	2–1000	14	0.59	32
alcohols + glycerol	298	4–290	9	0.58	52
ethylene glycol + glycerol	RT	50–1000	6	0.59	36
2-methyltetrahydrofuran	125–298	0.5–34	8	0.78	this work
ethyl acetate	295–341	0.3–0.4	10	1.00	14
dimethyl phthalate	297–396	1–14	14	0.49	14
glycerol	277–381	12–7100	19	0.73	14
glycerol	293–373	69–6800	18	0.71	48
7 imidazolium ionic liquids	263–343	10–700	11	0.35–.69	52

^a Exponents p derived from fits of approximate rates calculated from quantum yield data as described in the text to the forms $\ln(k_{\text{rxn}}/T) = A - p \ln(\eta)$. # indicates the number of data points in the fit. RT indicates room temperature.

friction often being weaker than the hydrodynamic prediction $(k_{\text{rxn}}/T) \propto \eta^{-1}$.

Returning to Figure 8, it is clear that viscosity alone is not the only factor influencing the rates of these reactions, as evidenced by the considerable spread among the different solvent classes for a given viscosity. For example, using the correlation lines in Figure 8, representative time constants for reaction ($\tau_{\text{rxn}} = 1/k_{\text{rxn}}$) of DMN at 25 °C and $\eta = 1 \text{ cP}$ are 0.9 ps in *n*-alkanes, 1.5 ps in *n*-alcohols, and 2.8 ps in aprotic solvents. The corresponding times for JDMN are 1.9, 2.8, and 4.0 ps. Given that solvent polarity generally increases in this same order, these variations suggest that the reaction rates might depend on solvent polarity. To examine this possibility, we attempted to fit the room-temperature solvent data to functions including both measures of solvent polarity and viscosity. As illustrated in Figure 10, reasonable fits could be achieved using the functional form:

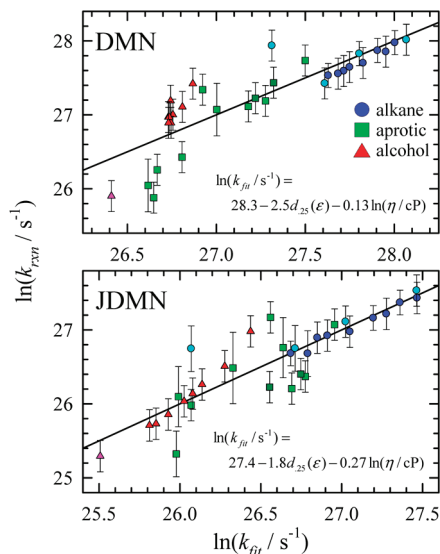


Figure 10. Correlation of the 25 °C reaction rates as a function of both solvent polarity and viscosity according to eq 12. In the case of the non-dipolar solvents dioxane and benzene a value of $\epsilon = 5$ was used. The standard errors in these fits are 0.32 (DMN) and 0.29 (JDMN). Symbols and colors are as defined in Figure 7.

$$\ln k_{\text{rxn}} = a + b d_{0.25}(\epsilon) + c \ln \eta \quad (12)$$

where $d_c(\epsilon)$ is the dielectric reaction field factor defined in eq 4. Use of b terms of the form $b \ln\{d_c(\epsilon)\}$ also provide similar quality representations of these data. Based on the relative magnitudes of the b and c terms derived from fits such as those in Figure 10, one would conclude that energetic (ϵ) and frictional (η) solvent contributions play comparable roles in determining the reaction rates at room temperature, and that energetic/polarity effects are relatively more important in DMN than in JDMN. For example, using the values of b and c from Figure 10 and the range of ϵ and η values spanned by these data, the relative rate variations in different solvents produced by $d_c(\epsilon)$ versus $\ln \eta$ terms is approximately 4:3 in DMN and 1:2 in JDMN. Given that the fits shown in Figure 10 only reproduce the data with standard errors of 30–40%, too much emphasis should not be placed on the quantitative conclusions drawn from such correlations. Furthermore, attempts to simultaneously fit the temperature-dependent data in Figure 9 and these room-temperature data in this manner are not satisfactory. Nevertheless, at least to the extent that viscosity is an adequate representation of solvent friction, these data indicate that the energetic effects of solvent polarity cannot be ignored. Reaction rates decrease as solvent polarity increases. The reasonable correlation achieved in terms of dielectric properties further suggests that specific solvation effects are not important in these reactions.

Two other observations support the idea of a decreasing reaction rate with increasing solvent polarity. The first is that substantial variations of the emission quantum yields and reaction rates of DMN and JDMN are observed as functions of excitation wavelength in ionic liquids⁵¹ and other solvents⁷⁵ whose solvation is slow compared to the rate of reaction. Excitation at different wavelengths, especially on the red edge of the absorption band, selects different subpopulations of the inhomogeneously broadened spectrum according to their relative solvation energies. Molecules absorbing on the low-energy side of the absorption band are those most strongly solvated, or alternatively those in the “most polar” environments. The fluorescence yield of these molecules is greater than average, meaning that these best-solvated molecules react more slowly

than molecules having average solvation energies. While we are still analyzing such experiments quantitatively, the qualitative conclusion is that increased solvation leads to slower reaction, consistent with the direction of the trend with solvent shown in Figure 8. This trend is also consistent with recent electronic structure calculations which show a significant decrease in the S_1 dipole moment (~ 5 D according to the best calculations) as a function of torsion angle.¹ How we envision this dipole moment variation might influence the S_1 potential energy surface and thereby modify reaction rates is shown in Figure 10. Differential stabilization of the Franck–Condon region ($\tau \sim 0^\circ$) relative to $\tau \sim 90^\circ$ due to the greater dipole moment near $\tau = 0^\circ$ could create a small barrier to reaction in more polar solvents as depicted here. Alternatively, this differential solvation could lessen a slightly downward slope of the nearly flat potential in the region $0 \leq \tau \leq 45^\circ$ or reduce the angular width of the “shelf” in polar versus nonpolar solvents. Whatever the scenario, the fact that rate variations only amount to a factor of 2–3 implies that these variations with solvent polarity cannot be much larger than thermal energies ($k_B T = 2.5$ kJ/mol). It could also be that the effect of solvent polarity is frictional rather than energetic. The malononitrile group is highly polar, and interactions with polar solvents could lead to greater friction compared to nonpolar solvents.

We now consider in more detail the nature of the solvent friction on these reactions and ask why the viscosity dependence observed is relatively weak, typically characterized by viscosity exponents well below unity. In doing so it is useful not only to examine the data measured here (Figures 8 and 9) but also to include analogous viscosity-dependence data previously reported for these reactions. The variability of quantum yields from different groups (Table 2) precludes direct use of the rates obtained in other studies. Fortunately, however, the viscosity exponents p defined by relations of the sort $(k_{\text{rxn}}/T) \propto \eta^{-p}$ should be more reliably compared, because they depend only on relative fluorescence intensity measurements. In Table 4 we therefore summarize the viscosity exponents measured here and deduced from available literature quantum yield data using fits similar to those shown in Figures 8 and 9.⁷⁶ The literature data include temperature-dependent quantum yields from the seminal work of Loutfy and Arnold¹⁴ and a few other groups,^{48,52} and room-temperature solvent series,⁴⁸ mainly mixtures of glycerol and other alcohols.^{32,36,52} In viewing these data it should be kept in mind that rate variations due to the effects of solvent polarity have not been accounted for and such effects might either reduce or increase the apparent value of p .⁷⁷ From Table 4 we find that the largest exponents, i.e. the behavior most closely approaching the hydrodynamic expectation $p = 1$, are found in the simple, nonassociated solvents MTHF and ethyl acetate. The smallest values of p occur for the n -alkane solvent series. Glycerol and solutions of other alcohols and glycerol consistently yield exponents with intermediate values of p near 0.6–0.7. But beyond these few observations it is difficult to discern any clear trends in the exponents observed with solvent type. The only obvious conclusion to be drawn from Table 4 is that the viscosity dependence of these reactions is nearly always weaker than hydrodynamic predictions with average values of p being 0.6 ± 0.2 .

We finally ask how this scaling with viscosity is best interpreted. Rates that scale as some fractional power of viscosity are well-known in a number of different contexts and have been interpreted in a variety of ways. Such behavior was first noted for isomerization reactions in early quantum yield measurements of the excited-state isomerization of stilbene derivatives,⁷⁸ where

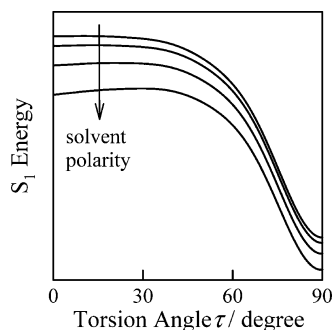


Figure 11. Schematic representation of the possible effect of solvent polarity on the reactive S_1 surface. Torsion angle here is the angle about the double bond undergoing isomerization. The topmost curve here is a fit to the gas-phase S_1 energy surface calculated using the model chemistry SA2-CAS(12,11)/6-31G(d).¹ The remaining curves are schematic.

it was interpreted in terms of free-volume ideas.^{79,80} Many more recent examples of excited-state^{81,82} and ground-state⁸³ isomerization reactions have also been reported to depend on viscosity in this manner. The most popular current explanations focus on the frequency dependence of friction on sharp barriers^{84,85} or on motions occurring on multidimensional potential surfaces.^{86,87} Fractional power-law dependence on viscosity is also observed for simple nonreactive dynamics. For example, recent reviews^{88,89} show that translational diffusion coefficients in a wide range of neat liquids and dilute solutions scale with η^{-p} with exponents typically in the range $0.7 \leq p \leq 1.0$. Rotational correlation times of both small^{90–92} and large^{93,94} solutes also exhibit such non-hydrodynamic behavior when viewed across a series of solvents such as the *n*-alkanes, despite showing the more expected behavior $\tau_{\text{rot}} = C(\eta/T) + \tau_0$ in single-solvent measurements.⁹⁵ In these nonreactive situations, lack of adherence to a $|p| = 1$ dependence has usually been interpreted in terms of changes in the coupling “ C ”, especially in series of different solvents.^{93,96–99}

Adopting the view that reaction rates in DMN and JDMN are determined by the times required for torsional motion on a flat potential to reach some reactive end point (i.e., the shelf “edge” beginning near 45° in Figure 11), of the phenomena mentioned above, solute rotation provides the closest analogue. For simplicity, we consider the rotating moiety to be the malononitrile group. Using an ellipsoid of semiaxis dimensions (a, b, c) = (3.5, 2.5, 1.8) Å to represent this group, the hydrodynamic prediction¹⁰⁰ for the time required to diffuse 45° about the y axis (the direction bisecting the two CN bonds) in a medium of viscosity 1 cP at 25 °C is 9.2 ps assuming stick conditions and 2.3 ps assuming slip boundary conditions. These predictions can be compared to the observed reaction times at 1 cP of 0.9–2 ps (DMN) and 2–4 ps (JDMN). Thus, the times for reaction are close to or slightly below the slip hydrodynamic predictions and much smaller than stick predictions. Such an observation is consistent with what is found for the rotation of small prolate molecules. Stick hydrodynamic predictions grossly overestimate observed times, and slip predictions provide reasonable estimates for rotation times observed in neat liquids,^{101,102} whereas times significantly smaller than slip predictions are observed in dilute solution when the solute is smaller than the solvent molecules.⁹² The closest comparisons available to the present data are the rotation times of CH_3CN measured in the neat liquid state and in *n*-alkane solvents by Tiffon and Ancian.⁹¹ These authors compared the observed rotation times of the $\text{C}\equiv\text{N}$ bond of CH_3CN to slip hydrodynamic predictions calculated using an ellipsoidal representation, as we

TABLE 5: Ratios of Observed Reaction Rates and Rotation Times to Slip Hydrodynamic Predictions^a

solvent	η/cP	$V_{\text{vdW}}/\text{\AA}^3$	$(V_u)/(V_v)$	$(\tau_{\text{rot}})/(\tau_{\text{slp}})$		$(k_{\text{slp}})/(k_{\text{rxn}})$	
				CH_3CN	DMN	JDMN	
<i>n</i> -pentane	0.21	96	0.49		1.4	2.2	
<i>n</i> -hexane	0.30	105	0.45	0.98	1.0	1.7	
<i>n</i> -heptane	0.39	130	0.36		0.89	1.5	
<i>n</i> -octane	0.51	147	0.32	0.85	0.67	1.2	
<i>n</i> -decane	0.84	181	0.26	0.64	0.48	0.87	
<i>n</i> -dodecane	1.37	215	0.22	0.49	0.31	0.56	
<i>n</i> -tridecane	1.71	232	0.20		0.26	0.47	
<i>n</i> -tetradecane	2.11	250	0.19	0.42	0.22	0.47	
<i>n</i> -hexadecane	3.05	283	0.17	0.32	0.16	0.32	
acetonitrile	0.34	47	1.00	1.5	1.7	1.8	

^a η and V_{vdW} are the solvent viscosity and the van der Waals volume of the solvent molecules.¹¹³ V_u/V_v is the ratio of van der Waals volumes of the “solute” (based on a $\text{CH}_2(\text{CN})_2$) to that of the solvent. τ_{rot} is the rotation time of the long axis of CH_3CN determined from ^{14}N NMR measurements,⁹¹ and k_{rxn} are the reaction times measured for DMN and JDMN. The latter values are shown as ratios to the predictions of hydrodynamics calculations using ellipsoidal representations for the rotating object (CH_3CN or $\text{CH}_2(\text{CN})_2$) and the slip boundary condition.¹⁰⁰

have done here. The ratios of observed/predicted times from this study are provided along with corresponding values estimated for reaction of DMN and JDMN in Table 5. As seen in Table 5 the observed/predicted ratios for this simple rotation process are remarkably similar to those associated with reaction. In most cases the CH_3CN rotation ratios fall between the ratios calculated for DMN and JDMN. The similarity of these ratios suggests that the weak viscosity dependence (small p values) observed in the DMN and JDMN isomerization reactions, at least within a homologous series such as the *n*-alkanes, is not qualitatively different from the decoupling from solvent viscosity seen in small molecule rotations. As the solute/solvent size ratio decreases below unity, the observed dynamics becomes increasingly faster relative to slip predictions because less and less solvent must be moved to allow the motion. Although a number of models explaining this departure from simple hydrodynamics have been proposed,^{96,103–105} none are entirely successful in reproducing experimental behavior and we do not attempt to apply such models to the present data. For now we merely conclude that frictional effects on these reactions appear to be closely related to friction on small-molecule rotations and leave it to future work to explore this connection further.

4. Summary and Conclusions

In this work we have surveyed the room-temperature spectroscopy and lifetimes of the two benzylidene malononitriles DMN and JDMN in relation to their use as probes of solvent friction. We found the spectroscopy of these molecules to be relatively uncomplicated. The lowest energy absorption band consists of a single well-isolated transition, and, apart from some change in Franck–Condon activity, emission occurs from the same state initially excited. The solvent dependence of absorption frequencies and bandwidths are readily understood in terms of dielectric models of solvatochromism, and this dependence reflects the substantial charge transfer character ($\Delta\mu \sim 8.5$ D) of the $S_0 \rightarrow S_1$ transition. Specific solvation effects such as hydrogen bonding do not appear to influence the spectra. Analysis of the emission solvatochromism of these molecules is complicated by the fact that emission typically does not originate from equilibrium solvation conditions due to the short lifetimes of S_1 .

Time-resolved emission spectra of DMN reveal a modest ($\sim 1000\text{ cm}^{-1}$) dynamic Stokes shift due to polar solvation. This shifting appears to be independent of the internal conversion process that leads to the short ($\sim 1\text{ ps}$) lifetimes of these molecules. Radiative rates, either estimated from absorption transition moments or measured from fluorescence lifetimes, show no significant dependence on solvent. Average values of $k_{\text{rad}} = 0.32 \pm 0.02\text{ ns}^{-1}$ (DMN) and $0.28 \pm 0.02\text{ ns}^{-1}$ (JDMN) can therefore be used along with fluorescence quantum yields to provide convenient measures of the rate of the excited state reaction (internal conversion). Reaction rates measured in this manner in 33 room-temperature solvents are consistently faster in DMN than in JDMN by a factor of 2.0 ± 0.2 .

We have interpreted the observed reaction rates in terms of a specific model of the excited-state reaction motivated by recent electronic structure calculations^{1,48} and associated simulations.¹ The model assumes reaction to occur on a nearly flat shelf-like potential and equates reaction to large-amplitude twisting about the double bond (c) in the absence of significant intramolecular forces. From this perspective, reactive motion is equivalent to the unforced rotation of a small molecule roughly the size of malononitrile ($\text{CH}_2(\text{CN})_2$) and the rate of this motion should be completely controlled by solvent friction. To the extent that solvent viscosity provides a valid measure of the relative magnitudes of friction in different solvents, the fact that we observe reaction rates that differ by factors of 2–3 in solvents of identical viscosity points out the incompleteness of this description. Correlations of reaction rates using viscosity to represent solvent friction and the dielectric constant to represent polarity suggest that solvent polarity is of comparable importance to friction in determining the solvent dependence of the observed rates. Given the large dipole moment of the S_1 state ($>17\text{ D}^2$), the existence of such a polarity dependence is not surprising. It can be accommodated within the basic picture described above by postulating that polarity changes cause minor deviations of the S_1 potential from an idealized shelf-like form. Alternatively the variations observed in different solvent classes might reflect frictional differences inadequately represented by equating friction with viscosity.

Within a single solvent as a function of temperature or in a series of solvents such as the *n*-alkanes, hydrodynamic theories predict $k_{\text{rxn}}/T \propto \eta^{-1}$. The rates measured here as well as the results compiled from prior studies show that reaction rates in DMN and JDMN actually vary as $k_{\text{rxn}}/T \propto \eta^{-p}$ with exponents *p* substantially less than unity, i.e. solvent frictional effects are much weaker than expected based on viscosity. No clear pattern in the exponent *p* with solvent characteristics is evident in the data collected thus far. Given the small volume swept out by twisting the malononitrile group, it is perhaps not surprising that the friction operative on these reactions is poorly described by solvent viscosity alone. But are there other solvent properties that would provide a more quantitative guide to solvent friction? In polymers, most workers have interpreted fluorescence yields in terms of the presence of unoccupied volumes of appropriate size to accommodate the reactive motion, rather than in terms of bulk viscosity.^{15,22} The same idea has been suggested for highly viscous liquids.¹⁴ Unfortunately, we have not found any more satisfactory representations of the rate data using free volume approaches.

For the moment at least, there is little choice but to rely on viscosity as the only simple measure of solvent friction and to seek a more molecular perspective on friction by understanding what factors cause deviations from hydrodynamic predictions. We noted that in most cases the observed reaction rates are not

too far from what would be expected based on the model described above and the friction predicted by slip hydrodynamics. We also found that deviations from hydrodynamic predictions as a function of solvent size observed in *n*-alkane solvents closely parallel those previously observed in the case of small-molecule rotations in these solvents. It might therefore prove useful to revisit the case of small-molecule rotations and make new measurements that can be more directly compared to the present data on reaction. The use of pressure as a variable was shown to provide useful insights into these reactions in polymer matrices,²⁷ and this technique should prove equally valuable for studying liquid solutions. Finally, computer simulations of the sort described in ref 1 should offer critical guidance for interpreting these experiments and help to build a more satisfying description of friction on such processes. We intend to pursue all three of these directions in future work.

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Supporting Information Available: Tables of DMN and JDMN solvatochromic and a figure showing plots of transition moments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (77) Because polarity increases along with viscosity as temperature is lowered, the exponents from temperature-dependent measurements are higher than they would be after removing the polarity effect. For example, if one subtracts a term $bd_c(\epsilon)$ from the temperature-dependent $\ln k_{\text{rxn}}$ data in Figure 9 using the value of b determined from fitting the room-temperature data to eq 11, in the viscosity exponents derived from this polarity-corrected data (assuming that the $d_c(\epsilon)$ term is Boltzmann weighted), the viscosity exponents decrease by about 25%. In contrast, in the series of n -alcohols at 25 °C, where viscosity and polarity change in opposite directions, correcting for polarity would tend to increase p .
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