The Photophysics of Three Naphthylmethylene Malononitriles

Jens Breffke,[†] Brian W. Williams,[‡] and Mark Maroncelli^{*,†}

[†]Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, United States [‡]Department of Chemistry, Bucknell University, Lewisburg, Pennsylvania 17837, United States

Supporting Information

ABSTRACT: The solvent dependence of the photophysical properties of three naphthylmethylene malononitriles, 1-(1-naphthalenylmethylene)-propanedinitrile (1-MN), 2-(2-naphthalenylmethylene)-propanedinitrile (2-MN), and 2-(3,4-dihydro-1(2H)-phenanthrenylidene)-propanedinitile (r2-MN), was studied in order to determine their potential utility as fluidity probes and to make comparisons to the better studied benzylidene malononitriles. Density functional calculations were used to understand the possible conformational states related to rotation about the vinyl-aromatic bond (" τ "). Absorption and emission frequencies, extinction coefficients, fluorescence quantum yields, and fluorescence lifetimes were measured in 11 representative solvents. Both the computational and experimental results indicate that the $S_0 \rightarrow S_1$ transitions of



these molecules have substantial charge-transfer character and produce highly polar excited states. Emission appears to result from relaxed S₁ states which do not differ qualitatively from the Franck–Condon states reached by absorption. In 2-MN, timeresolved emission reveals the presence of two ground-state conformers ("a" and "b" differing by ~180° rotation about τ) coexisting in low-polarity solvents. In contrast, 1-MN appears to exist primarily as a single dominant ground-state conformer. Fluorescence lifetimes vary from ~ 1 ps in 1-MN to ~ 200 ps in 2-MN(a) at room temperature. With the exception of 2-MN(a), the lifetimes vary systematically with solvent in a manner similar to what is observed in the benzylidene malononitriles. Both solvent polarity and fluidity appear to be important determinants of lifetime. The primary mechanism of fluorescence decay in naphthylmethylene malononitriles is likely to be the same as that of the benzylidene malononitriles—twisting about the double bond in S_1 , which leads to rapid internal conversion via a conical intersection with S_0 .

1. INTRODUCTION

Benzylidenemalononitriles are a class of molecules which have long been studied for their biological activity^{1,2} and fluorescence sensing properties.³⁻⁵ We have recently examined three such molecules, shown in the top row of Scheme 1, in



order to better understand the origins of their environmentally sensitive fluorescence.⁵⁻⁷ DMN and JDMN have been widely used as local fluidity sensors in a variety of contexts since the pioneering work of Law and Loutfy in the early 1980s.^{8,9} In low viscosity solvents, these molecules are weakly fluorescent, with fluorescence lifetimes in the few picosecond range,⁵ whereas in

high viscosity solvents¹⁰ or polymers¹¹ their fluorescence yields and lifetimes increase markedly.

Some disagreement still exists concerning whether the mechanism responsible for this environmental sensitivity is a twisted intramolecular charge transfer (TICT) process¹² involving rotation about the benzene-vinyl single bond (τ in Scheme 1) or a (null) "isomerization" about the double bond (ω). Computational work by our group⁶ and others^{13,14} favors the isomerization mechanism, which leads to a conical intersection between S₁ and S₀ and rapid internal conversion. In the asymmetric variant CCVJ, this mechanism can be verified experimentally because the isomerization leads to longlived photoproducts.7 (We note that CCVJ and related molecules have overshadowed DMN and JDMN as biological "rotor probes",^{15,16} but the potential presence of such photoproducts means that they must be used with caution.) Some support for the TICT mechanism was reported in a recent study of JDMN by Gaffney and co-workers.¹⁷ They found evidence that a long-lived TICT state may also be present in these molecules, at least when excited with

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Received: September 30, 2014 Revised: November 11, 2014 significant excess energy. Other work has made it clear that the fluorescence of DMN, JDMN, and CCVJ respond very similarly to environment,^{5,7,18} with both friction and polarity playing important roles.⁵ However, even in simple solvents, it remains unclear how one should interpret the often weak viscosity scaling and apparent polarity dependence of these "fluidity" sensors.

The present study seeks to provide additional perspective on such questions by exploring the photophysics and solvent sensitivity of several related molecules, depicted in the lower portion of Scheme 1. In these naphthylmethylene malononitriles, the dimethylaniline donor of the former probes is replaced by naphthalene. We anticipated that this change would significantly alter the details of the S₁ potential energy surface on which the reaction is expected to sensitively depend⁶ while maintaining their electronic spectra in an experimentally convenient range. The differences in electronic and steric interactions between the donor and acceptor groups in 1-MN versus 2-MN might also be expected to produce significantly different excited-state behavior in these two molecules. Finally, the conformational restrictions imposed in the variant r2-MN should eliminate the possibility of TICT state formation, providing additional perspective on the deactivation mechanism. In the present work, we provide the first systematic look at the electronic structures and photophysical properties of these molecules in a selected collection of solvents and relate their behavior to that of DMN and JDMN.

Compared to the extensive work on benzylidene malononitriles, only limited and sporadic attention has been paid to vinyl malononitriles with other aromatic donors. Three papers have reported systematic studies of such systems.^{19–21} In a brief note, Aihara et al.¹⁹ measured the absorption frequencies and extinction coefficients of a collection of nine aromatic malononitriles (Ar—CH==C(CN)₂) in chloroform. They observed a clear correlation between the frequencies of the lowest energy absorption bands and the ionization potentials of the aromatic subsystem, indicating that the (Franck–Condon) S₁ states of these molecules are of intramolecular charge transfer (ICT) character.

The most extensive study to date was performed by Katritzky et al.²⁰ who measured absorption and emission spectra of five Ar—CH==C(CN)₂ molecules with Ar = benzene, naphthalene (1-MN), phenanthrene, anthracene, and pyrene in a collection of eight solvents. They found that, whereas the absorption bands did not vary much with solvent polarity, the emission spectra did. They interpreted this observation as indicating that the emission comes from an ICT state which is distinct from the Franck–Condon state reached by absorption. They also noted the fluorescence of these molecules is very weak (quantum yields typically less than 10^{-3}), which led them to suggest that this ICT state was likely to be a TICT state, achieved by a 90° rotation about the aryl–vinyl bond.

In the most recent study, Wang et al.²¹ measured the emission spectra of 1-MN and the same anthracene and pyrene variants as Katritzky et al. in poly(methyl methacrylate) at pressures of up to nearly 80 kbar. They reported emission of all three solutes to consist of two distinct bands, which they interpreted as emission from a locally excited (LE) state and an ICT state. With increasing pressure, the intensity of the overall emission as well as the relative intensity of the ICT state increased dramatically. In the anthracene case, the main focus of their work, they observed the total emission intensity to increase approximately 100-fold and the ICT intensity by ~400-fold at 74 kbar relative to atmospheric pressure. Wang et al. analyzed this pressure dependence in terms of pressure affecting the relative populations of two ground-state conformers which independently give rise to the LE and ICT emission, rather than to an LE \rightarrow ICT reaction occurring in the excited state. However, we believe that this analysis and interpretation are incorrect. These authors neglected the fact that the 325 nm excitation used in their experiments excites into S₂ not S₁. On the basis of relative absorption and emission frequencies, it is clear that, rather than LE and ICT emission, what was being observed was emission from S₂ and S₁, with this violation of Kasha's rule being allowed by the very weak character of the S₁ emission even in a polymer host at low pressures.

Two additional studies should also be mentioned relative to the present work. Liu and co-workers²² measured the effect of UV irradiation on the absorption spectra of 2-MN and 1-MN in a 77 K glass in ordered to provide evidence for the "hula-twist" mechanism of isomerization.²³ In this mechanism, isomerization about a double bond is accomplished by concerted motion of the double bond and a neighboring bond in a manner that minimizes the volume required. This mechanism has a higher intrinsic activation energy than direct rotation about the isomerizing bond, but it may be preferred in rigidified media. In the case of 2-MN and 1-MN, the hula-twist mechanism converts an extended conformer into a more compact conformer ($\mathbf{a} \rightarrow \mathbf{b}$ in Scheme 2). Liu and co-workers





reported changes to the absorption spectra upon irradiation consistent with the hula-twist mechanism occurring in 1-MN. In 2-MN, either the change did not occur or the spectroscopic changes produced were too small to observe.

Finally, we note that the present work was initiated partly as a follow-up to a survey of the solvent dependence of the absorption and emission spectra of 2-MN and r2-MN by Donnovan²⁴ under the guidance of one of us (B.W.W.). This earlier study examined the solvatochromism of both of the solutes, and some of these prior results are comparable to what we report herein. However, on the basis of the present work, we now believe that the r2-MN emission data reported by Donnovan are incorrect due to the presence of low levels of a fluorescent impurity which dominated its very weak fluorescence. All of the results reported here have been collected subsequent to this earlier work and with independently synthesized solutes.

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

Solutes. 1-(1-Naphthalenylmethylene)-propanedinitrile (1-MN) was synthesized by Knoevenagel condensation^{25,26} as follows. 1-Naphthalenecarboxaldehyde (4.81 g; 30.8 mmol), propanedinitrile (2.16 g; 32.6 mmol), and zinc chloride (4.51 g; 33.1 mmol) were mixed and ground together. The mixture was placed in a glass test tube immersed in a boiling water bath, allowed to melt, and stirred occasionally for 20 min. The crude product was then dissolved in 5% aqueous ethanol, washed twice in diethyl ether, and dried overnight under a vacuum, resulting in 3.08 g of 1-MN (15.1 mmol; 49%). No further purification was required. ¹H NMR (300 MHz, CDCl₃): δ 7.711 (3H, m), 8.104 (1H, t), 8.296 (3H, m), 9.207 (1H, s). 2-(2-Naphthalenylmethylene)-propanedinitrile (2-MN) was synthesized similarly using 2-naphthalenecarboxaldehyde (2.36 g; 15.11 mmol), propanedinitrile (1.06 g; 16.04 mmol), and zinc chloride (2.15 g; 15.77 mmol). A 2.36 g portion of 2-MN (12.87 mmol; 85%) was obtained. ¹H NMR (300 MHz, CDCl₃): δ 7.701 (2H, m), 8.130 (4H, m), 8.484 (2H, m).

2-(3,4-Dihydro-1(2H)-phenanthrenylidene)-propanedinitile (r2-MN) was synthesized according to Ettenger et al.²⁷ using 3,4dihydro-1(2H)-phenanthreone (1.91 g; 9.73 mmol), propanedinitrile (2.10 g; 31.17 mmol), and sodium acetate (1.80 g; 21.94 mmol). Purification was done by column chromatography using 5% ethyl acetate in hexanes three times. A 0.24 g portion of r2-MN (1 mmol; 10%) was obtained. ¹H NMR (300 MHz, CDCl3): δ 2.260 (2H, m), 3.114 (2H, t), 3.438 (2H, t), 7.693 (2H, m), 7.930 (1H, d), 8.003 (1H, d), 8.170 (1H, d), 8.257 (1H, d). Unfortunately, even after three purification steps, a fluorescent impurity at the level of 1–2% remained in this sample. The impurity has a nanosecond lifetime, and its emission sufficiently dominated the steady-state emission of r2-MN that it was not suitable for steady-state emission experiments.

Solvents. Most solvents used were from Sigma-Aldrich and were of spectroscopic or HPLC grade. They were used as received except for some being dried over molecular sieves and filtered through a 0.45 μ m syringe filter prior use.

Spectroscopic Measurements. A Hitachi U-3010 UV/vis in combination with a SPEX Fluorolog FL212 spectrometer were used for steady-state absorption and emission measurements. Emission spectra were corrected with respect to spectral responsitivity using secondary emission standards.²⁸ Samples were prepared from a concentrated 1,4-dioxane stock solution $(\sim 0.01 \text{ M})$ and diluted at least 300-fold with the target solvent. At this level of dilution, we could not observe any effect of the dioxane on the spectral shapes, positions, or lifetimes. Measurements were carried out in 1 cm quartz cuvettes at concentrations providing ~1 OD for absorption spectra and <0.1 for emission spectra, quantum yields and single photon counting experiments. Temperature was set at 25 °C ± 0.1 using a water chiller circulating fluid through sample holders in all experiments except for the Kerr-gated experiments, which were at room temperature, 21 ± 2 °C. Deoxygenation did not have a noticeable effect, and therefore, most samples were not deoxygenated. Fluorescence quantum yields were measured relative to quinine sulfate in 0.05 M H₂SO₄ excited at 390 nm $(\varphi_{\rm em} = 0.508)^{29,30}$ and calculated according to³¹

$$\varphi_{\rm S} = \varphi_{\rm R} \left(\frac{n_{\rm S}^2}{n_{\rm R}^2} \right) \left(\frac{I_{\rm S}}{I_{\rm R}} \right) \left(\frac{A_{\rm R} \cdot 10^{-0.5 \cdot A_{\rm R}}}{A_{\rm S} \cdot 10^{-0.5 \cdot A_{\rm S}}} \right)$$
(1)

where n is the solvent refractive index, I the integrated emission intensity, and A the absorbance of the sample (S) and reference (R).

Time-resolved data were acquired using two different instruments. The first is a Kerr-gated emission (KGE) instrument with subpicosecond time resolution, which has been described in detail previously.³² The KGE system is based on a 250 kHz amplified Ti:sapphire laser system (Coherent Innova 400/Mira 900/RegA 9050) tuned to 775 nm with a power output of 1.5 W. Frequency doubling provided 387 nm light for excitation of the sample contained in a 0.5 mm flow cell. The fundamental was used to gate the emission in a 0.7 mm thickness cell of benzene which served as the Kerr medium. The instrumental response from this system was \sim 350 fs (fwhm) based on the solvent Raman signal. Data sets were time corrected for group velocity dispersion and intensity corrected for CCD responsitivity and gating efficiency. A deconvolution procedure was also applied in some cases to increase confidence in the kinetics observed at early times.

The time correlated single photon counting (TCSPC) technique employed here utilizes a cavity dumped Ti:sapphire oscillator (Coherent Mira 900+PulseSwitch) pumped by a CW laser (Coherent Verdi V-5) at 532 nm. Output pulses have a width of <300 fs at a variable repetition rate of 5.43 MHz or lower, and a tunable wavelength range of 760-900 nm. The mode-locked output of the laser is frequency doubled in a 2 mm BBO crystal. Beam intensity is attenuated by an adjustable $\lambda/2$ plate in front of a Glan-Thompson polarizer to provide vertical polarization with restricted excitation energy to ensure single photon collection. The system allows alignment of the excitation beam for either right angle or front face detection. Emission from the sample passes through an optical filter to remove scattered excitation light and a Glan-Thompson polarizer. Finally, the emission is spectrally resolved using a 100 mm single grating monochromator (Instruments SA, Inc. H-10) with a 4 nm band-pass prior to detection with a 6 μ m microchannel plate photomultiplier (MCP-PMT; Hamamatsu, R3809U). The MCP-PMT signal is amplified (Becker & Hickl HFAC-26) and sent to a photon counting module (Becker & Hickl SPC-130) on which the constant fraction discriminator, time-to-amplitude converter (TAC), analog-to-digital converter, data processing logic, and data memory are integrated. Photon counting acquisition is operated in a reversed startstop mode in which an emission photon triggers the TAC and a delayed reference pulse from a photodiode (Optoelectronics PD-30) is used to synchronize a termination signal. The instrument response function determined by a scattering solution is typically 25 ps fwhm. The experiments performed here utilized 380–390 nm excitation light, right angle collection from a 1 cm square cuvette, a GG-400 optical filter to reject scattered excitation light, and magic angle detection.

Computational Methods. Several quantum chemical methods were used to study the molecular structures and photophysical properties relevant to the excited-state dynamics. Most calculations involved time-dependent density functional theory (TDDFT) with the B3LYP and CAM-B3LYP functionals and a 6-31G(d,p) basis set. Møller–Plesset perturbation theory (MP2) was also used to obtain an S₀ molecular geometry for comparison to X-ray structures and the B3LYP results. Solvent effects were explored using implicit solvent calculations with the polarizable continuum model.³³ Most calculations were performed using Gaussian 09.³⁴ For exploring the nature of the excited-state potential upon rotation about the

Table 1. Calculated Ground-State Properties^a

| molecule | method | $\Delta E ~(\mathrm{kJ}~\mathrm{mol}^{-1})$ | ΔG (kJ mol ⁻¹) | au (deg) | θ (deg) | ω (deg) | μ (D) |
|----------|--------|---|------------------------------------|----------|----------------|----------------|-----------|
| 2-MN(a) | B3LYP | (0) | (0) | 0 | 131.6 | 0.0 | 7.7 |
| | MP2 | (0) | (0) | 6 | 130.6 | 0.0 | 6.6 |
| 2-MN(b) | B3LYP | 1.4 | 0.8 | 180 | 131.7 | 0.0 | 7.2 |
| | MP2 | 0.5 | 5.7 | 156 | 128.4 | 0.0 | 6.0 |
| r2-MN | B3LYP | | | -26 | 124.4 | 2.9 | 7.7 |
| | MP2 | | | -34 | 122.8 | 1.9 | 6.5 |
| 1-MN(a) | B3LYP | (0) | (0) | 27 | 129.9 | 3.1 | 7.1 |
| | MP2 | (0) | (0) | 43 | 125.8 | 3.2 | 5.8 |
| 1-MN(b) | B3LYP | 12.9 | 13.3 | 138 | 130.6 | 2.3 | 6.5 |
| | MP2 | 5.8 | 5.5 | 131 | 126.4 | 2.0 | 5.3 |

 ${}^{a}\Delta E$ is the difference in electronic energy and ΔG is the difference in the Gibbs free energy (298 K) relative to the lowest energy conformer. τ , θ , and ω are the angles defined in Scheme 2, and μ is the dipole moment.

double bond, a few spin-flip TDDFT calculations^{35–37} were also performed using the GAMESS³⁸ electronic structure program. For these calculations Minezawa's method³⁶ and the BHHLYP hybrid functional with the Dunnin–Hay double- ζ plus polarization DH(d,p) basis set were used.

3. RESULTS AND DISCUSSION

A. Electronic Structure Calculations. 1-MN and 2-MN can exist as two conformers which differ by rotation around the malononitrile single bond, defined by torsion angle τ . As shown in Scheme 2, we label the more extended conformer "**a**" ($\tau \sim 0^{\circ}$) and the other conformer "**b**" ($\tau \sim 180^{\circ}$). Results of ground-state optimizations originating from initial $\tau = 0$ and 180° geometries are compiled in Table 1.

We first consider 2-MN. For this isomer, DFT (B3LYP/6-31G(d,p) calculations predict both conformers **a** and **b** to be planar and to have virtually identical energies and dipole moments. MP2/6-31G(d,p) calculations predict either a small (2-MN(a), 6°) or moderate (2-MN(b), 25°) degree of nonplanarity caused by repulsion between one CN group and a ring H atom. This repulsion is partly alleviated by an opening of the vinyl angle θ (Scheme 2). No crystal structure of 2-MN is available for comparison, but experimental data are available for the related molecules benzylidene malononitrile (BzMN) and 2-vinylnapthalene (2-VN). Spectroscopic studies of 2-VN suggest that the a conformer is planar but are indecisive concerning the b conformer.³⁹ Similarly to 2-MN, B3LYP calculations predict both conformers of BzCN to be planar, whereas MP2 calculations predict nonplanar forms, $\tau(\mathbf{a}) = 15^{\circ}$ and $\tau(\mathbf{b}) = 150^{\circ}$. In the crystal, BzMN is nonplanar, $\tau =$ 11°, $(\tau = 0^\circ)$ and MP2 ($\tau = 23^\circ$) predictions bracket this value. Other comparisons to BzMN Xray data are provided in Table S1 of the Supporting Information. On the basis of these comparisons, we conclude that 2-MN(a) is likely to be planar or nearly so in the ground state, whereas 2-MN(b) is probably twisted by a moderate angle, comparable to the 11° twist measured for BzMN. Both model chemistries predict only a slightly lower energy for the a conformer and nearly equal dipole moments for the two conformers. On this basis, we expect both the a and b conformers of 2-MN to be significantly populated in the roomtemperature experiments conducted here.

The ground-state potential energy profile of 2-MN as a function of the torsion angle τ is shown in Figure 1a. Because of the possibility of TICT state formation in S₁, we performed torsional scans using both the B3LYP functional (black circles) and its Coulomb attenuated version,⁴³ CAM-B3LYP (red



Figure 1. Relative potential energies as functions of the single bond torsion angle τ calculated at the levels B3LYP/6-31G(d,p) (black circles) and CAM-B3LYP/6-31G(d,p) (red triangles). (a) 2-MN in S_0 , (b) 1-MN in S_0 , (c) 2-MN in S_1 , and (d) 1-MN in S_1 . These profiles were made by fixing the dihedral angle shown in bold in Scheme 2 and optimizing all other coordinates. S_1 profiles are TDDFT calculations. Energies were calculated over the entire range $0-360^\circ$ and symmetry related values at τ and $360 - \tau$ averaged. Error bars indicate twice the difference between these two energies.

triangles). In the ground state, similar results are obtained using these two functionals. Both show barriers to interconversion of **a** and **b** conformers to be ~30 kJ/mol in 2-MN, which is considerably larger than the barrier in 2-VN (10-20 kJ/mol).³⁹

r2-MN was synthesized as a torsionally restricted analogue of 2-MN(a), and we will show that it shares many spectroscopic features in common with 2-MN (a or b). Nevertheless, joining the naphthalene ring and malononitrile groups in this way renders r2-MN significantly nonplanar, $\tau \sim 30^{\circ}$ (Table 1). This nonplanarity relieves some of the strain on the vinyl angle, allowing θ to decrease, but it also causes some twisting of the C=C bond, denoted by ω (see Scheme 2).

In the case of 1-MN, steric repulsion leads to both \mathbf{a} and \mathbf{b} conformers being significantly nonplanar (Table 1; see also Figure 3). The \mathbf{a} conformer is calculated to be preferred in the gas phase, and it is the form found in the crystalline state,⁴⁴

| Table 2. E | xcited-State and | Transition Pr | operties from | TD (| Calculations at t | the S_0 | Geometries ^{<i>a</i>} |
|------------|------------------|----------------------|---------------|------|-------------------|-----------|--------------------------------|
|------------|------------------|----------------------|---------------|------|-------------------|-----------|--------------------------------|

| molecule | functional | | $(D)^{\mu_1}$ | $\begin{array}{c} \vec{\mu}_1 - \vec{\mu}_0 \\ (D) \end{array}$ | $\nu_{1 \leftarrow 0} (10^{3} \text{ cm}^{-1})$ | | $f_{1\leftarrow 0}$ | $(D)^{\mu_2}$ | $\begin{array}{c} \vec{\mu}_2 - \vec{\mu}_0 \\ (D) \end{array}$ | $\nu_{2 \leftarrow 0} (10^{3} \text{ cm}^{-1})$ | $\begin{array}{c} M_{2\leftarrow 0} \\ (\mathrm{D}) \end{array}$ | $f_{2\leftarrow 0}$ |
|----------|------------|-----|---------------|---|---|-----|---------------------|---------------|---|---|--|---------------------|
| 2-MN(a) | B3LYP | 7.7 | 15.0 | 7.5 | 26.5 | 3.3 | 0.13 | 10.8 | 3.2 | 30.9 | 6.5 | 0.62 |
| | CAM-B3LYP | 7.4 | 13.5 | 6.2 | 31.3 | 4.4 | 0.29 | 10.5 | 3.2 | 34.1 | 5.8 | 0.55 |
| 2-MN(b) | B3LYP | 7.2 | 14.6 | 7.5 | 25.3 | 2.9 | 0.10 | 9.8 | 2.7 | 30.3 | 5.8 | 0.48 |
| | CAM-B3LYP | 6.9 | 13.0 | 6.3 | 30.1 | 4.0 | 0.23 | 9.9 | 3.0 | 33.5 | 5.0 | 0.39 |
| r2-MN | B3LYP | 7.7 | 14.5 | 7.4 | 26.1 | 3.1 | 0.12 | 10.3 | 3.0 | 30.6 | 5.6 | 0.44 |
| | CAM-B3LYP | 7.5 | 12.8 | 5.9 | 30.9 | 4.1 | 0.25 | 9.9 | 3.0 | 34.2 | 4.8 | 0.36 |
| 1-MN(a) | B3LYP | 7.1 | 13.2 | 6.2 | 26.0 | 4.8 | 0.29 | 13.4 | 6.3 | 30.7 | 1.4 | 0.03 |
| | CAM-B3LYP | 6.8 | 12.2 | 5.5 | 30.3 | 5.3 | 0.40 | 10.8 | 4.1 | 35.2 | 1.3 | 0.03 |
| 1-MN(b) | B3LYP | 6.5 | 11.8 | 6.1 | 25.8 | 4.1 | 0.21 | 12.1 | 6.2 | 30.8 | 1.2 | 0.02 |
| | CAM-B3LYP | 6.1 | 11.6 | 6.1 | 30.4 | 4.4 | 0.28 | 9.4 | 3.7 | 35.4 | 1.0 | 0.02 |

 ${}^{a}\mu_{i}$ is the permanent electric dipole moment of state S_{i} , i = 0, 1, 2, and $|\vec{\mu}_{i} - \vec{\mu}_{0}|$, $\nu_{i \leftarrow 0}$, $M_{i \leftarrow 0}$ are the change in dipole moment, the transition energy, the transition dipole moment, and the oscillator strength of the $i \leftarrow 0$ transition.

where $\tau = 38^{\circ}$. In light of the calculated energy differences and its larger dipole moment (see below), it seems likely that 1-MN(a) is the dominant ground-state conformer in solution. In this conformer, there is also a modest twist about the double bond, predicted to be $\omega \sim 3^{\circ}$ by DFT and MP2 calculations and measured to be $\omega \sim 5^{\circ}$ in the crystal.⁴⁴ The torsional potential of 1-MN (Figure 1b) shows a slightly smaller barrier separating the **a** and **b** conformers than in 2-MN, but the overall barrier to 180° rotation is comparable. Comparisons to available X-ray data on 1-MN⁴⁴ and r2-MN²⁷ (Supporting Information, Tables S2 and S3) indicate slightly greater accuracy for the DFT predictions of S₀ properties, and we will primarily focus on these calculations in the remainder of the discussion.

Characteristics of the lowest energy electronic transitions and electric dipole moments based on gas-phase TDDFT calculations are summarized in Table 2. Additional calculations including implicit solvent are provided in Table S4 of the Supporting Information. In all molecules/conformers, both functionals predict S_1 to be separated from S_2 by 2900–5000 cm⁻¹. Vertical transition energies ($\nu_{1\leftarrow0}$, $\nu_{2\leftarrow0}$) calculated with the CAM-B3LYP functional are all 3200-4800 cm⁻¹ larger than the B3LYP calculations. As far as these transition energies are concerned, the B3LYP calculations are the more realistic. Figure 2 compares experimental absorption spectra in *n*-hexane to gas-phase B3LYP calculations. As illustrated here, the B3LYP calculations are in reasonable agreement with experiment as regards the frequencies and relative oscillator strengths of the low-energy transitions. The same is true in the case of r2-MN, whose transition properties are close to those of 2-MN(a). Selfconsistent reaction field calculations in cyclohexane (Table S4, Supporting Information) are similar to those shown in Figure 2 but with the S_1 and S_2 transitions red-shifted by about 800 cm⁻¹. The comparison between experiment and CAM-B3LYP calculations (Figure S1, Supporting Information, and Table 2) is much poorer; all transition frequencies are calculated higher than observed. As will be seen later, the transition strengths calculated using CAM-B3LYP are also in poorer agreement with experiment. Thus, the Coulomb attenuation correction is not helpful for describing these transitions, despite their partial charge-transfer character. We will therefore focus on the B3LYP calculations henceforth. A final observation to be made on the basis of Figure 2 (and Table 2) is that these calculations predict that it would be difficult to distinguish between the a and b conformers of either 2-MN or 1-MN in the experimental spectra.45



Figure 2. Experimental absorption spectra in *n*-hexane (smooth curves) compared to gas-phase TD-B3LYP-calculated vertical excitation energies and oscillator strengths (bars) of 2-MN and 1-MN. The first six $S_0 \rightarrow S_n$ transitions are shown. **a** and **b** conformer calculations are shown in blue and red, respectively. The vertical scales of the experimental spectra are arbitrary.

The dipole moments listed in Table 2 indicate all molecules/ conformers to be significantly more polar in S₁ than in S₀. The increase in polarity results from transfer of electron density from the naphthalene ring to the vinyl malononitrile group. Ground-state dipole moments are all 7–8 D, and as illustrated in Figure 3, they are in all cases oriented from the malononitrile group to the naphthalene ring. These dipole moments suggest significant charge transfer is present in the ground state. Mulliken and ESP-fit atomic charges⁴⁶ both indicate the naphthalene ring to be positive by 0.17–0.21*e* in all cases. The S₁ – S₀ differences, $|\vec{\mu}_1 - \vec{\mu}_0|$, entail loss of an additional ~0.3*e* from the naphthalene ring, so that there is approximately a net charge separation of 0.5*e* in the S₁ state. In the case of 2-MN, the S₂ state is of intermediate polarity compared to S₀ and S₁, whereas in 1-MN the S₁ and S₂ states are of similar polarity.

Figure 3 also indicates the directions of the electric transition dipole moments between S₀, S₁, and S₂ (B3LYP calculations at the S₀-optimized geometries). In 2-MN, the S₀ \rightarrow S₁ and S₀ \rightarrow S₂ transition moment directions ($\vec{M}_{1\leftarrow 0}$ and $\vec{M}_{2\leftarrow 0}$) are within 25° of one another, with the stronger S₂ transition lying closer to the ring-malononitrile direction. In 1-MN, the S₀ \rightarrow S₁



Figure 3. Directions of the S_0 state permanent electric dipole $(\mu_0, green)$ and transition dipole moments of the transitions $S_0 \rightarrow S_1$ $(\vec{M}_{1\leftarrow0}, red)$ and $S_0 \rightarrow S_2$ $(\vec{M}_{2\leftarrow0}, blue)$. Geometries and μ_0 are from B3LYP/6-31G(d,p) calculations of S_0 , and transition moments are from TD-B3LYP calculations at the S_0 geometry.

transition is also aligned with the ring–malononitrile direction (close to $\vec{\mu}_0$), but in this case, the $S_0 \rightarrow S_1$ transition is closer to orthogonal to this direction, lying along the long naphthalene axis.

The molecular orbitals and main configurations comprising the S_1 and S_2 states are summarized in Figure S2 and Table S5 (Supporting Information). As noted by Pfanstiel and Pratt concerning 2-VN, the π orbitals of 1-MN (a or b) resemble those of naphthalene much more than do those of 2-MN (a or b) or r2-MN, which are more like those of a linear polyene including the malononitrile group. In all cases, the S_1 state is comprised mainly of the HOMO \rightarrow LUMO excitation, which is not purely charge-transfer in character.

We finally consider the relaxed S_1 torsional potentials displayed in the bottom panels of Figure 1. In contrast to the S₀ potentials, the predictions of the B3LYP (black) and CAM-B3LYP (red) calculations differ significantly. In 2-MN, the primary minima in S₁ still lie near $\tau = 0$ and 180°, but the barrier separating these minima is much larger in the CAM calculations, >35 kJ/mol vs ~5 kJ/mol. Whereas the B3LYP calculations suggest that conformer interconversion might be possible during the lifetime of S₁, the CAM-B3LYP predictions preclude such interconversion. In the case of 1-MN, the B3LYP calculations predict a global minimum near 90°, and a state significantly different in character from the Franck-Condon (FC) states of 1-MN(a) or 1-MN(b) (see Table S4, Supporting Information). Whereas all of the other S₁-optimized geometries have dipole moments and transition properties close to those at their respective FC geometries, this $\sim 90^{\circ}$ state is predicted to have a dipole moment ~4 D larger, and much weaker and largely red-shifted emission, hallmarks of a twisted intramolecular charge transfer (TICT) state. The B3LYP torsional profile in S₁ is such that Franck–Condon excitation of 1-MN(a or b) would lead to a rapid conformational change to this TICT state. In contrast, no TICT state or important torsional relaxation is predicted by the CAM calculations. As discussed later, we believe the CAM calculations are more consistent with experiment in regard to the shape of the S_1 potential surface.

B. Steady-State Spectra and Solvatochromism. Steadystate absorption and emission spectra were recorded in a series



Figure 4. Absorption and emission spectra of 1-MN and 2-MN in five solvents of varying polarity. Solvents are *n*-hexane, di-*n*-butylether, methyl acetate, methanol, and acetonitrile.

of 11 solvents. Representative data are shown in Figure 4. The spectra of r2-MN closely resemble those of 2-MN (Figure S3, Supporting Information) and are therefore not included here. As already seen in Figure 2, the absorption spectra of 2-MN above 300 nm $(34\,000 \text{ cm}^{-1})$ appear to consist of two overlapping bands, whereas those of 1-MN appear as a single peak. On the basis of the calculations of the previous section, we interpret the absorption of 2-MN in terms of a slightly structured S₁ absorption centered near 27 000 cm^{-1} and a stronger, less structured S₂ absorption near 30 000 cm⁻¹. Both of these absorption bands are likely to contain contributions from closely spaced 2-MN(a) and 2-MN(b) conformers. The calculations of the previous section suggest that the properties of the two conformers are similar, and in the present section, we treat them as an effective average species. The lowest energy absorption band of 1-MN is attributed to a single electronic transition from the single conformer 1-MN(a). As illustrated in Figure 4, the absorption bands of both compounds shift to the red with increasing solvent polarity. The emission spectra of 1-MN and 2-MN are similar in shape. In weakly polar solvents, vibronic structure is observed, but this structure is largely obscured in solvents of even moderate polarity. The emission bands shift considerably more with solvent polarity than do the absorption bands, and the shift is larger in 2-MN compared to 1-MN.

In order to quantitatively analyze solvent-induced shifts and other spectral parameters of the absorption of 2-MN and r2-MN, it is necessary to effect an approximate separation of their overlapping S_1 and S_2 absorption bands. As illustrated in Figure 5 for the case of 2-MN, this separation is performed by assuming that the overlapping bands can be fit by a sum of two log-normal line shape functions:⁴⁷

$$L(\nu) = \begin{cases} h \exp\{-\ln(2)[\ln(1+\alpha)/\gamma]^2\} & \text{for } \alpha > -1 \\ 0 & \text{for } \alpha < -1 \end{cases}$$
(2)



Figure 5. Decomposition of the lowest-frequency band of 2-MN (black crosses) into approximate S_1 (green) and S_2 (red) contributions. The heavier black curves at the bottom of the lower panels are the residuals, differences between the observed and fit relative absorbance. These residuals are shown on expanded scales in the top panels ($\pm 2\%$).

where $\alpha = 2\gamma(\nu - \nu_0)/\Delta$. The parameter γ defines the asymmetry of the band, ν_0 is the peak frequency, and Δ is a width parameter related to the full width at half-maximum Γ by $\Gamma = \Delta \sinh(\gamma)/\gamma$. In highly polar solvents like acetonitrile, all eight parameters $\{h_i, \nu_{0,i}\Gamma_i, \gamma_i \text{ for } i = 1, 2\}$ are reasonably determined. In less polar solvents and especially in nonpolar solvents like *n*-hexane, the structure present in the S₁ absorption cannot be captured by a log-normal function, and as a result, the parameters cannot all be determined with confidence. To achieve consistent and sensible representations for all solvents studied, we fixed the following parameters to the average values observed in polar solvents: $\Gamma_1 = 4000 \text{ cm}^{-1}$, $\gamma_1 = 0.38$, and $\gamma_2 = 0.26$. We believe that such fits afford relative absorbances accurate to $\pm 10\%$ and first-moment frequencies

$$\langle \nu \rangle = \nu_{\rm pk} + \frac{\Delta}{2\gamma} \left[\exp\left(\frac{3\gamma^2}{4\ln 2}\right) - 1 \right]$$
 (3)

accurate to 300 cm⁻¹ (S₁) or 50 cm⁻¹ (S₂).

Summaries of solvent-dependent frequencies of 2-MN and 1-MN are provided in Tables 3 and 4, and analogous results for r2-MN are presented in Table S6 (Supporting Information). Peak frequencies ν_{pk}^{abs} and extinction coefficients ε_{mx} are those directly measured from the spectra, i.e., without separating S₁ and S₂. In 2-MN and r2-MN, first moment frequencies in absorption $\langle \nu_{abs}^{(1)} \rangle$ and $\langle \nu_{abs}^{(2)} \rangle$ are from the log-normal fits (eq 3), whereas those for 1-MN and those reported for the emission of all solutes are numerically integrated values.

To quantify and partially interpret the solvent dependence of the solvatochromic shifts, we employ a simple polarizable point dipole solute + dielectric continuum solvent model described previously in refs 5 and 48. Within this model, absorption and emission frequencies are related to the refractive indices n_D and relative permittivities ε_r of solvents according to

$$\nu_{abs,em} = \nu_{abs,em}^{0} + A_{abs,em} d_c (n_D^2) + C_{abs,em}$$
$$\times [d_c(\varepsilon_r) - d_c(n_D^2)]$$
(4)

with

$$d_{c}(x) = (x-1)/\{2(1-c)x + (1+2c)\}$$
(5)

The factors $d_c(n_D^2)$ and $[d_c(\varepsilon_r) - d_c(n_D^2)]$ characterize the electronic and nuclear (total minus electronic) polarizabilities of the solvent, and ν^0 , A, and C are related to solute properties, as is the constant c, which is proportional to its electronic polarizability.^{48,5} Here we choose c = 0.25 and use the factors d_c to correlate observed shifts. (Solvent properties, including these $d_{c'}$ are provided in Table S7, Supporting Information.)

Fits of $\langle \nu_{abs}^{(l)} \rangle$ to eq 4 are shown in Figure 6, and all regression equations are summarized in Table S8 (Supporting Information). Note that toluene has been omitted from these fits because the permittivity of this primarily quadrupolar solvent poorly represents its total polarizability in relation to molecular solvation.^{49,50} As illustrated by the spread of points in the top panel of Figure 6, the solvent sensitivity of the S₁ absorption bands to solvent increases in the order 1-MN < 2-MN < r2-MN. The difference between 1-MN and 2-MN is anticipated on the basis of the larger S₀ and S₁ dipole moments calculated for 2-MN (Table 2), but the even larger solvent sensitivity of r2-MN and the larger size of r2-MN. The much smaller solvent

Table 3. Solvent-Dependent Photophysical Properties of 2-MN $(25 \text{ °C})^a$

| # | solvent | $ u_{ m pk}^{ m abs}$ | $\varepsilon_{\rm mx}$ | $\langle u_{ m abs}^{(1)} angle$ | $M_{1\leftarrow 0}$ | $\langle u_{ m abs}^{(2)} angle$ | $M_{2\leftarrow 0}$ | $\langle \nu_{\rm em} \rangle$ | $\varphi_{\rm em}~(10^{-3})$ | $\langle \tau_{\rm em} \rangle$ | $k_{ m rad}$ | $M_{1 \rightarrow 0}$ | $	au_{\mathrm{a}}$ | $	au_{\mathrm{b}}$ |
|----|---------------------|-----------------------|------------------------|------------------------------------|---------------------|------------------------------------|---------------------|--------------------------------|------------------------------|---------------------------------|--------------|-----------------------|--------------------|--------------------|
| 1 | n-hexane | 30.53 | 27.0 | 28.33 | 3.2 | 31.26 | 5.2 | 24.05 | 4.8 | 128 | 3.75 | 2.1 | 257 | 21 |
| 2 | n-heptane | 30.47 | 27.3 | 28.29 | 3.2 | 31.22 | 5.2 | 24.04 | 5.3 | 135 | 3.90 | 2.2 | 248 | 22 |
| 3 | cyclohexane | 30.36 | 27.2 | 28.20 | 3.3 | 31.12 | 5.2 | 23.95 | 5.3 | 98 | 5.42 | 2.5 | 184 | 18 |
| 4 | di-n-butyl ether | 30.37 | 26.1 | 28.06 | 3.3 | 31.08 | 5.2 | 23.25 | 7.0 | 115 | 6.08 | 2.8 | 146 | 39 |
| 5 | diethyl ether | 30.46 | 27.1 | 28.07 | 3.3 | 31.16 | 5.3 | 22.86 | 8.3 | 119 | 6.97 | 3.2 | 147 | 39 |
| 6 | methyl acetate | 30.49 | 26.1 | 28.02 | 3.3 | 31.20 | 5.3 | 21.99 | 7.3 | 136 | 5.33 | 3.0 | 136 | |
| 7 | 1-pentanol | 30.22 | 27.1 | 27.78 | 3.5 | 30.95 | 5.4 | 21.87 | 7.0 | 164 | 4.24 | 2.6 | 164 | |
| 8 | propylene carbonate | 30.30 | 24.5 | 27.76 | 3.4 | 31.02 | 5.2 | 20.97 | 9.4 | 166 | 5.67 | 3.2 | 166 | |
| 9 | acetonitrile | 30.48 | 25.7 | 27.93 | 3.3 | 31.17 | 5.3 | 21.09 | 7.7 | 154 | 5.00 | 3.1 | 154 | |
| 10 | methanol | 30.43 | 26.7 | 27.88 | 3.4 | 31.13 | 5.4 | 20.90 | 7.8 | 154 | 5.05 | 3.2 | 154 | |
| 11 | toluene | 29.88 | 22.5 | 27.72 | 3.3 | 30.76 | 5.0 | 22.36 | 5.4 | 121 | 4.49 | 2.4 | 154 | |

 ${}^{a}\nu_{pk}^{abs}, \langle \nu_{abs}^{abs} \rangle, \langle \nu_{abs}^{2bs} \rangle$, and $\langle \nu_{em} \rangle$ are the frequencies of the peak of the S₁+S₂ absorption band and the first moment frequencies of the S₁ and S₂ bands and the emission, respectively, all in units of 10³ cm⁻¹. ε_{mx} is the decadic molar absorption coefficient of the S₁+S₂ band at the maximum in units of 10³ M⁻¹ cm⁻¹, the $M_{i \leftrightarrow j}$ are the transition dipole moments of the $i \leftrightarrow j$ transition in D, and φ_{em} is the emission quantum yield. $\langle \tau_{em} \rangle$ is the average decay time and τ_a and τ_b the component decay times observed in biexponential fits in units of ps, and k_{rad} is the (average) radiative rate in units of 10⁷ s⁻¹.

Table 4. Solvent-Dependent Photophysical Properties of 1-MN $(25 \ ^{\circ}C^{a})^{b}$

| # | solvent | $ u_{ m pk}^{ m abs}$ | $\varepsilon_{\rm mx}$ | $\langle u^{(1)}_{ m abs} angle$ | $M_{1 \leftarrow 0}$ | $\langle \nu_{\rm em} \rangle$ | $\varphi_{\rm em}~(10^{-4})$ | $\langle \tau_{\rm em} \rangle$ | $k_{ m rad}$ | $M_{1 \rightarrow 0}$ | $\langle \tau_{\nu} \rangle$ |
|----|---------------------|-----------------------|------------------------|------------------------------------|----------------------|--------------------------------|------------------------------|---------------------------------|--------------|-----------------------|------------------------------|
| 1 | <i>n</i> -hexane | 27.40 | 13.2 | 28.63 | 4.4 | 23.10 | 1.9 | 0.52 | 3.67 | 7.1 | |
| 2 | n-heptane | 27.35 | 13.3 | 28.56 | 4.5 | 22.98 | 1.9 | 0.64 | 2.96 | 6.4 | |
| 3 | cyclohexane | 27.25 | 13.2 | 28.49 | 4.5 | 22.93 | 2.1 | 0.84 | 2.52 | 5.8 | |
| 4 | di-n-butyl ether | 27.18 | 12.4 | 28.38 | 4.4 | 22.52 | 1.1 | 0.87 | 1.31 | 4.4 | |
| 5 | diethyl ether | 27.28 | 12.6 | 28.49 | 4.5 | 22.28 | 2.3 | 0.91 | 2.57 | 6.4 | |
| 6 | methyl acetate | 27.46 | 11.6 | 28.71 | 4.5 | 21.55 | 2.2 | 1.7 | 1.24 | 4.7 | 0.41 |
| 7 | 1-pentanol | 26.99 | 12.1 | 28.22 | 4.6 | 21.70 | 1.9 | 1.7 | 1.11 | 4.2 | 3.0 |
| 8 | propylene carbonate | 27.23 | 11.1 | 28.51 | 4.5 | 20.75 | 3.3 | 2.7 | 1.22 | 4.7 | 1.7 |
| 9 | acetonitrile | 27.44 | 11.6 | 28.70 | 4.5 | 20.79 | 2.2 | 1.9 | 1.15 | 4.8 | 0.13 |
| 10 | methanol | 27.32 | 10.8 | 28.59 | 4.4 | 20.97 | 2.7 | 1.41 | 1.90 | 6.2 | 6.1 |
| 11 | toluene | 26.73 | 11.4 | 27.93 | 4.3 | 21.82 | 2.2 | 0.84 | 2.62 | 6.1 | |

^{*a*}Lifetime data are at 21 ± 2 °C rather than 25 °C. ${}^{b}\nu_{pk}^{abs}$ and $\langle\nu_{abs}\rangle$ are the peak and first moment frequencies of the S₁ absorption band, and $\langle\nu_{em}\rangle$ is the first moment frequency of the emission band in units of 10³ cm⁻¹. ϵ_{mx} is the maximum decadic molar absorption coefficient of the S₁ band in units of 10³ M⁻¹ cm⁻¹, the $M_{i \leftarrow j}$ are the transition dipole moments of the $i \leftrightarrow j$ transition in D, and φ_{em} is the emission quantum yield. $\langle\tau_{em}\rangle$ is the average time associated with the emission intensity decay and $\langle\tau_{\nu}\rangle$ the time associated with the frequency shift of the emission spectrum in units of 10⁸ s⁻¹.



Figure 6. Correlations of first-moment absorption band frequencies according to eqs 4 and 5. Filled red symbols denote 2-MN, open green symbols r2-MN, and filled blue symbols 1-MN. Circles denote aprotic and squares alcohol solvents. Toluene data are omitted. These regressions are the best linear or bilinear regressions shown in boldface in Table S8 (Supporting Information).

sensitivity of the S_2 absorption bands of 2-MN and r2-MN compared to S_1 is as expected based on the smaller calculated S_2 dipole moments (Table 2), but the greater sensitivity of r2-MN compared to 2-MN is again unexpected.

Using the solvatochromic model above, rough estimates of the change in the (gas-phase) dipole moments between S₁ and S₀, $\Delta \mu = |\vec{\mu}_1 - \vec{\mu}_0|$, can be determined from the observed Stokes shifts via^{48,5}

$$\nu_{\rm abs} - \nu_{\rm em} = (\nu_{\rm abs}^0 - \nu_{\rm em}^0) + \frac{2(\Delta\mu)^2}{a^3} [d_{\rm c}(\varepsilon_{\rm r}) - d_{\rm c}(n_{\rm D}^2)]$$
(6)

where a is the radius of the effective spherical cavity representing the solute. In Figure 7, plots of the Stokes shifts of 2-MN and 1-MN are provided. (Corresponding data on r2-MN could not be obtained due to interference from impurity emission.) As illustrated in Figure 7, good linear correlations



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Figure 7. Stokes shifts of 2-MN (red) and 1-MN (blue) versus the solvent nuclear polarizability factor $d_c(\varepsilon_r) - d_c(n_D^{-2})$. Circles denote aprotic and squares alcohol solvents. The asterisk marks 1-MN in 1-pentanol.

are found between $(\nu_{\rm abs} - \nu_{\rm em})$ and the solvent nuclear polarizability $d_{\rm c}(\varepsilon_{\rm r}) - d_{\rm c}(n_{\rm D}^{-2})$; values of r^2 are 0.99 (2-MN) and 0.90 (1-MN). The poorer fit in the case of 1-MN is due to the 1-pentanol datum (asterisk in Figure 7). As will be seen later, 1-MN lifetimes are short (~1 ps), and because 1-pentanol solvates much more slowly ($\sim 100 \text{ ps}^{51}$) than the remaining solvents, the steady-state emission of 1-MN is not equilibrated, an assumption implicit in eq 6. The slopes of the fits in Figure 7 are 5900 cm⁻¹ (2-MN) and 4900 cm⁻¹ (1-MN). The value of $\Delta \mu$ derived from these slopes is highly dependent upon the choice of cavity radius a. Plausible values of a range between 3.6 Å, the radius of a sphere equal to the van der Waals volume of the solute (188.8 Å³ based on van der Waals increments⁵²), and this value augmented by the radius of a typical solvent molecule (~2.5 Å). These values, a = 3.6-5.1 Å, yield values of $\Delta \mu =$ 11.4–5.1 D for 2-MN and $\Delta \mu$ = 10.4–4.7 D for 1-MN. The TD-B3LYP/6-31G(d,p) calculated values are $\Delta \mu = 6.7$ D for 2-MN and 6.0 D for 1-MN. Thus, the calculated values are consistent with the observed solvatochromism of these molecules.

Katritzky et al.²⁰ previously measured the solvatochromism of 1-MN but in a smaller collection of solvents (only six omitting the quadrupolar solvents toluene and dioxane). Using a = 3.7 Å and neglecting any dependence of ν_{abs} on solvent, these authors estimated $\Delta \mu = 3.2$ D. A slightly different analysis of these same data by Ravi et al.⁵³ using the same value of *a* later produced a slightly larger value $\Delta \mu = 3.9$ D. Both values fall significantly below the already large range of values $\Delta \mu =$ 10.4–4.7 D derived here for 1-MN. The difference is partly due to assumptions made in the analysis, but it is also due to differences in the spectroscopic data. Obtaining reliable emission data for 1-MN is difficult because of its low emission quantum yield, and the differences may reflect the effect of impurities in the emission data.⁵⁴

C. Transition Dipole Moments. Quantities related to the strength of the $S_0 \leftrightarrow S_1$ and $S_0 \rightarrow S_2$ transitions of these molecules are provided in Tables 3 and 4 and Table S6 (Supporting Information). Maximal absorption coefficients ε_{mx} for the S_1/S_2 composite bands of 2-MN and r2-MN average 2.6 $\times 10^4$ and 2.2 $\times 10^4$ M⁻¹ cm⁻¹, respectively, whereas that of the S_1 band of 1-MN is roughly half of these values, 1.2×10^4 M⁻¹ cm⁻¹. Previously reported values of ε_{mx} are 2.81 $\times 10^4$ M⁻¹ cm⁻¹ (2-MN) and 1.42×10^4 M⁻¹ cm⁻¹ (1-MN) in chloroform¹⁹ and 1.4×10^4 M⁻¹ cm⁻¹ for 1-MN in tetrahydrofuran.²⁰

For quantitative comparison to calculated transition strengths, we compute transition dipole moments via $^{55-57}$

$$|\vec{M}_{I\leftarrow0}|^{2} = \frac{1}{n_{\rm D}f(n_{\rm D})} \left[\frac{2303}{8\pi^{3}} \frac{3hc}{N_{\rm A}} \right] \int_{\rm band\,I} \frac{\varepsilon(\nu)}{\nu} \, \mathrm{d}\nu \tag{7}$$

with

$$f(x) = \frac{9x^2}{(2x^2 + 1)^2}$$
(8)

where h, c, and N_A are Planck's constant, the speed of light, and Avogadro's number. For separating the S_1 and S_2 absorption bands, we used the log-normal fits described in the previous section. Solvent data for 2-MN and r2-MN are plotted as functions of the total solvent polarity measure $d_c(\varepsilon_r)$ in Figure 8. Experimental values of $M_{1\leftarrow 0}$ average 3.3, 3.3, and 4.5 D in 2-



Figure 8. Absorption (filled symbols) and emission (open symbols) transition dipole moments plotted as functions of the total solvent polarizability factor $d_c(\varepsilon_r)$. Circles denote aprotic solvents, squares alcohols, and the hexagon toluene.

MN, r2-MN, and 1-MN, respectively. These values are in excellent agreement with gas-phase TD-B3LYP/6-31G(d,p) calculations, which predict 3.1, 3.1, and 4.8 D (Table 2). Average values of the $S_0 \rightarrow S_2$ transition moments are 5.2 D in 2-MN and 4.7 D in r2-MN. These quantities are overestimated by the TDDFT calculations, which predict 6.2 and 5.6 D, respectively. The absorption transition moments of 2-MN and r2-MN appear to increase slightly with increasing solvent

polarity. The change is in all cases less than 10% over the full range of $d_c(\varepsilon_r)$. In the case of 1-MN, the change is negligible. We have also determined emission transition moments $(M_{1\to 0})$ of 2-MN and 1-MN using^{58,55}

$$|\vec{M}_{1\to 0}|^2 = \frac{1}{n_{\rm D}^3 f(n_{\rm D})} \left[\frac{3hc^3}{64\pi^4} \right] \frac{k_{\rm rad}}{\tilde{\nu}_{\rm em}^3}$$
(9)

In this expression, $k_{\rm rad}$ is the radiative rate, calculated from the emission quantum yield $\varphi_{\rm em}$ and average emission decay time $\langle \tau_{\rm em} \rangle$ via $k_{\rm rad} = \varphi_{\rm em} / \langle \tau_{\rm em} \rangle$, and $\tilde{\nu}_{\rm em}^{3} = \{ \int F(\nu) \, d\nu / \int F(\nu) \nu^{-3} \, d\nu \}$ with $F(\nu)$ being the emission spectrum (ν in s⁻¹). Values of $M_{1\rightarrow 0}$ for 2-MN and 1-MN are shown in Figure 8 (open symbols). The large error bars here reflect the difficulty associated with accurately measuring quantum yields in the range $10^{-4}-10^{-3}$ as well as uncertainties in the lifetime measurements. In the case of 1-MN, the emission transition moments average 5.5 \pm 1.0 D, compared to 4.5 \pm 0.1 D in absorption. Typically, emission transition moments are slightly smaller than absorption moments for well-isolated transitions. We suspect that the apparently larger average value of $M_{1\rightarrow 0}$ here as well as the scatter may reflect the presence of long-lived impurities. In the case of 2-MN, the average values are more in keeping with expectations: $M_{1\rightarrow 0} = 2.8 \pm 0.4$ D versus $M_{1\leftarrow 0} =$ 3.3 ± 0.1 D. There is, however, an unexpectedly large variation of $M_{1\rightarrow 0}$ with solvent, 40% over the range of solvents considered. The time-resolved data discussed in the next section indicate that the two conformers of 2-MN have markedly different lifetimes and their relative populations vary substantially with solvent polarity. It may be that this variation in conformer populations is somehow responsible for the variations in $M_{1\to 0}$ observed here.

D. Time-Resolved Emission. As indicated by the ~30-fold difference in quantum yields of 2-MN and 1-MN (Tables 3 and 4), the lifetimes of these molecules differ substantially. For this reason, different techniques were used to measure time-resolved emission.

In the case of 2-MN, lifetimes are on the order of 100 ps, sufficiently slow that time-correlated single photon counting (TCSPC) is able to faithfully record the emission dynamics. In most solvents studied, the decay kinetics observed using TCSPC were independent of emission wavelength. The main exception was 2-MN in 1-pentanol, where multiexponential wavelength-dependent kinetics were observed. We attribute this behavior to dynamic Stokes shifting of the emission due to solvation dynamics slow enough to be registered by the 25 ps time resolution of TCSPC. (The average solvation time in 1pentanol is ~100 ps.⁵¹) A ~5 ps lifetime component was detected on the blue side of the emission spectrum in methanol, which we also ascribe to solvation dynamics. In other solvents, we observed either single-exponential emission decays with time constants in the 100-300 ps range or biexponential decays with one component in this same range and another component between 20 and 50 ps. The latter behavior is observed only in the least polar solvents, the alkanes and ethers (#1-5). The amplitude of the short component decreases with increasing solvent polarity, from $\sim 50\%$ in nhexane to $\sim 25\%$ in diethyl ether.

We attribute the biexponential decay kinetics of 2-MN in low-polarity solvents to the coexistence of two conformers (**a** and **b**) with distinct lifetimes in these solvents. Evidence for this hypothesis is provided in Figure 9, where we show emission of 2-MN in *n*-hexane monitored at 420 nm as a function of



Figure 9. Excitation-wavelength-dependent emission decays of 2-MN in *n*-hexane. The left panel shows the absorption spectrum with excitation wavelengths indicated. The right panel shows emission decays collected at 420 nm. Decays were collected to 10⁴ counts in the peak channel except for the 400 nm decay, which was collected to 5000 counts and rescaled for comparison. "IRF" labels the instrument response function.

excitation wavelength. The left panel shows the red edge of the absorption spectrum with the excitation wavelengths indicated. Between 390 and 400 nm, a subtle change in the slope of the absorption edge suggests the possible presence of a weaker transition underlying the primary absorption. Excitation at 390 nm (used for most TCSPC experiments) or redder wavelengths greatly enhances the amplitude of the short (22 ps) component relative to the long (280 ps) component. The latter dominates the emission (70-80%) when excitation is at wavelengths shorter than 385 nm. On the basis of the TDDFT calculations (Figure 2), we tentatively assign the short lifetime component to emission from the b conformer and the long component to emission from the a conformer. Assuming approximately equal oscillator strengths, as suggested by calculation, these data indicate $\sim 25\%$ of the 2-MN adopts the b conformer in nhexane at 25 °C. This relative population is consistent with TDDFT energy calculations in cyclohexane (Table S4, Supporting Information). In solvents more polar than the alkanes, the absorption band shifts to the red such that 390 nm excitation is no longer on the edge of the absorption where it emphasizes b emission. Nevertheless, we would expect to be able to observe an ~25% amplitude fast component in the TCSPC decays if one were present. The fact that we fail to observe a shorter component in solvents more polar than diethyl ether suggests that the a conformer becomes increasingly favored with increasing solvent polarity, such that in methyl acetate and more polar solvents it contributes negligibly to the emission of 2-MN. Such a change with solvent is also supported by the DFT calculations in Table S4 (Supporting Information).

The emission lifetimes of 1-MN are all considerably shorter than those of 2-MN, and Kerr-gated emission (KGE) was therefore used to monitor emission dynamics. Representative spectra of 1-MN in acetonitrile are shown in Figure 10 to illustrate the analyses employed. Figure 10a shows "raw" spectra after correction for temporal dispersion and detection sensitivity. The sharp features at times comparable to the instrument resolution (350–400 fs fwhm) are solvent Raman bands. The raw spectra exhibit both a rapid intensity decay and a frequency shift over the course of a few picoseconds. To partially remove the effects of instrumental broadening from the results, these raw spectra were thinned and fit to a 4exponential model, resulting in the deconvoluted spectra shown Article



Figure 10. KGE spectra of 1-MN in acetonitrile showing (a) "raw" data (prior to deconvolution) and (b) spectra after thinning, conversion to frequency, and multiexponential fitting to remove instrumental broadening (points). The solid curves in part b are lognormal fits to the data. The dashed curve is the 10 ps spectrum renormalized to highlight the spectral shift.

in panel b. The latter spectra (points) were fit to log-normal functions (time-dependent versions of eq 5) excluding the Raman region. These fits are shown as the smooth curves in Figure 10b; they are used to provide simple metrics of the spectral evolution. Two spectral characteristics obtained in this manner, the integral intensities and peak frequencies of 1-MN in three solvents, are shown in Figure 11. In all three solvents,



Figure 11. Characteristics of the spectral evolution of 1-MN emission in acetonitrile, propylene carbonate (PC), and methanol. The left panel shows the decay of integral emission intensity and the right panel the peak frequency.

the intensity decays are significantly nonexponential. In highly polar solvents such as those illustrated, peak frequencies shift by $1500-2000 \text{ cm}^{-1}$. This shift is also nonexponential in time and occurs on a time scale comparable to the intensity decay. The widths of the spectra (not shown) decrease from ~5000 to ~4000 cm⁻¹ over this same time range. We fit both the intensity and frequency decays to biexponential functions of time to extract the integral times listed in Table 4. No obvious correlation exists between the times associated with the loss of emission intensity $\langle \tau_{\rm em} \rangle$ and the peak shift $\langle \tau_{\nu} \rangle$. Rather, in four

of the five solvents where comparisons are possible, the peak shift times are close to the Stokes shift times measured with the coumarin 153 (C153) probe.⁵¹ These observations suggest that the spectral shift is due to polar solvation and is not closely tied to the process leading to loss of emission. The exception is 1-pentanol, where the value of $\langle \tau_{\nu} \rangle$ obtained here (~3 ps) appears unrelated to the time associated with C153 solvation (~100 ps). This discrepancy is likely the result of the short lifetime of 1-MN (2 ps) obscuring the dominant slow solvation time constants ($\tau > 20 \text{ ps}^{51}$) present in 1-pentanol.

The lifetimes of r2-MN fall in the range 5-20 ps, intermediate between those of 2-MN and 1-MN. Due to the very limited amount of r2-MN available, we only measured its dynamics using TCSPC, which requires much less sample than the KGE experiment. Given the fact that the lifetimes of r2-MN are smaller than the 25 ps instrument response function, only an overall time constant associated with the emission decay could be determined. These lifetimes, which are averages over decays measured at four to five emission wavelengths, are collected in Table S6 (Supporting Information). It should be noted that the impurities which preclude accurate determination of the steady-state emission of r2-MN do not influence these lifetime data. In the TCSPC data, the impurities are manifest as a 1-2% component with a lifetime of ~ 3 ns. Although the difference in the r2-MN and impurity lifetimes means that impurities dominate the steady-state spectra, the opposite is true of the TCPC data, where the r2-MN component constitutes 98% or more of the decay amplitude.

We finally take an empirical look at the solvent dependence of the lifetimes observed for all three solutes. We consider three quantities potentially relevant to the emission deactivation process: the total solvent polarizability function, $d_{\rm c}(\varepsilon_{\rm r})$, the solvent viscosity η , and the average emission lifetime of the benzylidene malononitriles DMN and JDMN, τ_{BzMN} . (Because prior work showed a high degree of correlation between the lifetimes of DMN and JDMN,⁵ we use the average value here to represent this class of molecule.) The function $d_c(\varepsilon_r)$ is expected to be relevant to the decay kinetics if some polaritydependent barrier controls the deactivation. The viscosity, a coarse measure of solvent friction, is expected to be relevant if deactivation is controlled by some large amplitude motion through solvent. Finally, if the same mechanism of relaxation controls the fluorescence of the naphthalene and benzylidene malononitriles, one might expect au_{BzMN} to correlate the observed solvent dependence.

Figure 12 displays the lifetimes of 2-MN and 1-MN as functions of these three quantities. Consider first 2-MN. The decay time τ_{a} , attributed to the dominant **a** conformer of 2-MN, is approximately constant for most solvents except the alkanes, where it is significantly larger. As indicated by the small values of the coefficients of determination $("r^{2"})$ in Figure 12 (top values), none of the three quantities examined here explains most of the variance in τ_a with solvent. In the case of τ_b , attributed to 2-MN(b), decay times are most strongly correlated to $d_{\rm c}(\varepsilon_{\rm r})$, they exhibit a slightly weaker correlation to τ_{BzMN} and they appear unrelated to viscosity. The same pattern is observed in the case of the integral decay times of 1-MN. The strongest correlation is found with $d_c(\varepsilon_r)$, and the weakest correlation with η . As shown by the dashed line of equality ("1:1") in Figure 12, in 7 out of the 11 solvents studied, the intensity decay times of 1-MN are nearly equal to $\tau_{\rm BzMN}$ but in the 4 other solvents, the 1-MN lifetimes are significantly shorter than those of the benzylidene malononi-



Figure 12. Decay times plotted as functions of the total polarizability factor $d_c(\varepsilon_r)$, the solvent viscosity η , and the average decay time estimated for benzylidene malononitriles $\tau_{\rm BzCN}$ (see text). Circles denote aprotic solvents, squares alcohols, and the hexagon toluene. Inset numbers are the coefficients of determination of linear fits to the data. In the case of 2-MN, the top values are for τ_a (filled points) and bottom values τ_b (open symbols) regressions. The two small points in the top panel are 2-MN (τ_a) data for the additional solvents CH₂Cl₂ ($\tau_a \sim 100 \text{ ps}$) and ethyl acetate. These points are not included in the correlations.

triles. Finally, in the case of r2-MN, the decay times correlate moderately well with all three of these quantities ($r^2 = 0.5 - 0.6$).

4. SUMMARY AND CONCLUSIONS

We conclude by discussing the nature of the emitting states and origins of the short lifetimes of these naphthalene malononitriles in light of the results collected here as well as those available in the literature. The two studies to previously investigate emission in these molecules described the emission of 1-MN (and several other Ar-CH=C(CN)₂ systems) as reflecting the presence two distinct excited states, a locally excited (LE) state and an ICT state having much greater intramolecular charge transfer character.^{20,21} The time-resolved spectra of 1-MN and the other solutes recorded here indicate that excitation into S_1 leads to emission from only a single excited state. Comparisons between absorption and emission transition dipole moments (Figure 8) indicate that the absorbing and emitting states do not differ markedly. Although the solvent dependence of the emission moments of 2-MN is puzzling (and those of 1-MN scattered), these data are inconsistent with the idea that emission arises from a TICT state, as was originally suggested.²⁰

Calculations predict the ground-state dipole moments of all three solutes to be large, in the range 6–8 D. The solvent dependence of the Stokes shifts observed here (Figure 7) suggests that their S₁ state dipole moments are substantially higher, $\Delta\mu > 5$ D. These estimates are consistent with values of $\Delta\mu$ from TDDFT calculations, which all fall into the range 5–8 D (Table 2). Thus, the S₁ state can be reasonably described as an ICT state, as previously suggested. However, calculations indicate that the charge transfer is only partial—the naphthalene ring is already positive by $\sim 0.2e$ in S₀, and this charge only increases to $\sim 0.5e$ in S₁.

2-MN and 1-MN can exist as two ground-state conformers which differ in the torsional angle τ between the naphthalene ring and the vinylmalononitrile units. In both cases, the more extended a form (Scheme 2) is preferred. Calculations suggest that in 2-MN the conformers are sufficiently close in energy that both forms would be expected to be present in roomtemperature samples, whereas in 1-MN the energy difference is sufficiently great that the a conformer is expected to dominate (Table 1). In both 2-MN and 1-MN, the electronic properties of the two forms are calculated to be sufficiently similar (Figure 2, Table 2) that it would be difficult to distinguish them on the basis of their absorption or emission spectra. Time-resolved emission of 2-MN does, however, reveal the presence of two emitting species with distinct lifetimes in low polarity solvents. We interpret this behavior in terms of a ground-state equilibrium in which the slightly more polar a form begins to dominate as solvent polarity increases.

Like the benzylidene malononitriles, the lifetimes of all three of these naphthalene malononitriles are short and indicative of some fast excited-state process leading to a nonfluorescent state. In 2-MN and 1-MN, one cannot rule out the possibility that this process involves a TICT mechanism, i.e., twisting about τ to a virtually dark state at $\tau \sim 90^{\circ}$. B3LYP calculations suggest that such a state might represent a minimum on the S₁ potential energy surface (PES) of 1-MN. In contrast, CAM-B3LYP calculations (Figure 1) do not predict a TICT state, even in the presence of polar solvent (Table S4, Supporting Information) As discussed previously in regard to calculations on DMN,⁶ it is likely that the presence of this minimum is an artifact. The fact that r2-MN, which cannot undergo a TICT process, behaves similarly to 2-MN and 1-MN also argues against a TICT mechanism. Instead, it seems more likely that the fluorescence deactivation mechanism operative here is the same as that in DMN and JDMN-"isomerization" about the double bond which leads to an intersection between S_1 and S_0 near $\omega = 90^{\circ}$. We did not pursue multiconfigurational calculations of the sort needed to adequately explore the S₁ potential energy surfaces of these molecules with respect to this coordinate. However, preliminary spin-flip TDDFT calculations^{35–37} did demonstrate the presence of such a conical intersection at large ω .

Assuming this common mechanism, the question remains why significant differences exist among the lifetimes of these molecules: $2-MN(a) (\sim 100 \text{ ps}) > 2-MN(b) (\sim 30 \text{ ps}) > r2-MN$ $(\sim 10 \text{ ps}) > 1$ -MN $(\sim 1 \text{ ps})$. No definitive conclusions are possible at this point, but a few observations can be made. First, if one views these differences as resulting from changes to energy barriers along the reaction coordinate, factors of 10 equate to barrier height variations of ~6 kJ/mol (~2 $k_{\rm B}T$ at room temperature). Thus, one might reasonably ascribe these variations in lifetime to rather subtle differences in their S1 PESs (differences which would be hard to capture with current electronic structure methods). Second, there are structural differences among the three solutes with respect to the torsion angle τ , which might give rise to such differences in the S₁ PES. Although we believe that the excited-state reaction is directly related to twisting about ω rather than τ , it is reasonable to assume that these two angles are coupled. If the MP2 predictions are taken as the best estimators of ground-state geometries, one finds the torsion angle τ to vary in inverse

order to the lifetimes: 2-MN(a) (6°) < 2-MN(b) (25°) < r2-MN (34°) < 1-MN(a) (43°). In some cases, relief of the steric interference reflected in these τ angles also results in some nonplanarity of the double bond ($\omega \neq 0$) in the ground-state. MP2 calculations indicate $\omega = 0$ for both conformers of 2-MN, whereas in r2-MN and 1-MN this angle has been measured to be ~1 and ~6°, respectively.^{27,44} Thus, there is a correlation between twisting of the τ angle, which is perhaps accompanied by some slight nonplanarity of the double bond in the ground state, and the rate of the excited-state reaction. A similar correlation between the ground-state τ angle and barriers to excited-state isomerization in styrene derivatives was previously noted by Lewis and Zuo.⁵⁹

With the exception of 2-MN(a), these naphthalene malononitrile reactions display a solvent dependence not unlike those previously found for the benzylidene malononitriles DMN and JDMN.⁵ For the collection of 11 solvents considered here, we find that the lifetimes of 2-MN(b), r2-MN. and 1-MN all show significant correlations $(r^2 > 0.5)$ with the average lifetimes of DMN and JDMN (Figure 12), which are themselves strongly correlated. It therefore seems reasonable to conclude that the origins of the solvent dependence are similar. Despite the poor correlations with viscosity in Figure 12, we expect solvent friction to be one important factor controlling the lifetimes and emission yields of these molecules, as it is in the benzylidene malononitriles. Evidence comes from the ability to greatly enhance the emission yields upon environmental rigidification by either temperature⁶⁰ or pressure²¹ variation. The weak correlation with solvent viscosity observed here is likely a manifestation of the fact that solvent viscosity is a poor indicator of the friction operative on these reactions, at least when one considers an assortment of different solvents as was done here. In addition, solvent polarity, which provides some of the best correlations observed here (Figure 12), also appears to play a role in determining the solvent dependence of both classes of fluorophores, making them imperfect as simple reporters of fluidity. Disentangling frictional and energetic effects on these reactions is a challenging task, one which must await further investigation.

ASSOCIATED CONTENT

S Supporting Information

Comparisons of ground-state geometries predicted by B3LYP and MP2 calculations to X-ray data, tabulations of additional DFT calculations, descriptions of the frontier orbitals of all solutes, solvent-dependent photophysical properties of r2-MN, solvent properties, results of solvatochromic regressions, and comparisons of the absorption spectra of 2-MN and r2-MN. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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According to the work of Toptygin, this particular form is best justified by empirical evidence.⁵⁶ Use of this factor for the present collection of solvents increases the transition moments by an average of $17 \pm 2\%$ over using $f(n_D) = 1$, as in our prior work. (Note that the same local field factors are discussed in refs 55 and 56 but the notation differs slightly. Here we follow the notation in the former study.)

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Ν