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PAPER

2,5-PRODAN: synthesis and properties

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The preparations of 1-(6-(dimethylamino)naphthalen-1-yl)propan-1-one (2,5-PRODAN, **2**) and 7-(dimethylamino)-2,3-dihydrophenanthren-4(1H)-one **3** are described. The photophysical properties of these compounds are characterized and compared with those of PRODAN. Both compounds show solvatochromism that is similar in magnitude to PRODAN with a quantum yield that is nearly one order of magnitude smaller. Emission occurs from a locally excited (LE) state with charge-transfer character. There is no internal conversion to a different charge-transfer state as is seen in PRODAN.

Introduction

PRODAN, 6-propionyl-2-dimethylaminonaphthalene (**1**; Fig. 1), is a popular fluorophore that finds use as a molecular probe of polarity. Weber and Ferris prepared PRODAN in 1979, and showed that it binds to bovine serum albumin at a site with a polarity similar to that of methanol.¹ Placing the dimethylamino group and the propionyl group at positions 2 and 6, respectively, on a naphthalene ring, maximizes their separation while maintaining direct resonance. The mechanism by which PRODAN senses polarity is thought to be due to an intramolecular charge transfer (ICT) excited state. We have shown through a series of model compounds that this ICT state is likely to be planar (PICT)^{2–4} rather than twisted (N-TICT and/or O-TICT),^{5,6} although this view is not universally accepted. Placing the donor and acceptor groups in different positions might change the photophysical properties of the fluorophore. This paper reports the preparation and properties of two PRODAN derivatives **2** and **3** where the carbonyl group occupies the site corresponding to the 5-position in PRODAN. The fluorescence behavior of these two compounds is compared with that of PRODAN.

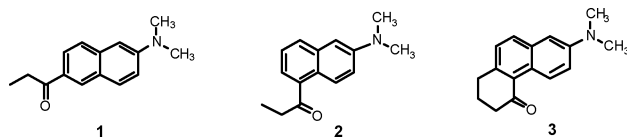
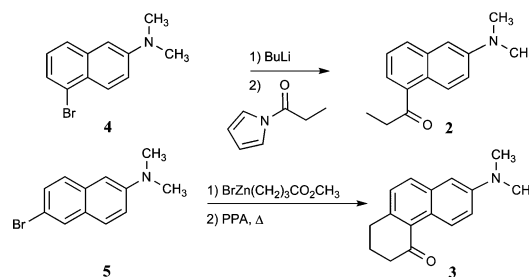


Fig. 1 Structure of PRODAN (**1**) and derivatives **2** and **3**.

Results and discussion

Synthesis

The preparation of **2** and **3** is shown in Scheme 1. The bromonaphthalene precursors **4** and **5** have been synthesized previously.^{7,8}



Scheme 1 Preparation of **2** and **3**.

Use of the acyl pyrrole reagent allows for the direct formation of the carbonyl group from the aryl lithium in the top reaction. The bottom reaction sequence is a Negishi coupling followed by cyclization of the terminal methyl ester in polyphosphoric acid that gives exclusive substitution at the α -position of the naphthalene ring. The proton NMR spectra of **2** and **3** show an unusual downfield shift of the peri-H proximal to the carbonyl group.

Photophysical studies

The solvatochromism of **2** and **3** is determined through their absorption and emission spectra in a variety of solvents. The absorption spectra show a moderate long-wavelength band near 390 nm (Table 1). This absorption is red-shifted by more than 30 nm from the corresponding band in PRODAN in nonpolar solvents. Unlike PRODAN the absorption bands shift very little with increasing solvent polarity.⁹ The large apparent shift in PRODAN has been attributed to two close-lying absorption bands.⁵ The emission spectra show significant solvatochromism (Fig. 2). Changing the solvent from cyclohexane to DMSO results in a red-shift of nearly 90 nm. A similar shift is seen in PRODAN. Solvent polarity affects the relative emission intensity. For PRODAN, the maximum emission intensity occurs in very polar solvents like DMSO, whereas for **2** and **3**, the maximum intensity occurs in nonpolar solvents like toluene and chlorobenzene. Relative quantum yields in toluene for **2** and **3** were 0.25 ± 0.07 and

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Table 1 Photophysical characteristics of PRODAN (**1**), **2** and **3**

Solvent	1			2			3		
	Abs.	em.	I/I_{\max}	Abs.	em.	I/I_{\max}	Abs.	em.	I/I_{\max}
C ₆ H ₁₂	343	392	0.01	379	437	0.64	397	449	0.72
PhMe	349	416	0.32	381	471	1.00	403	478	1.00
PhCl	354	440	0.75	381	488	0.95	402	498	0.96
EtOAc	352	456	0.85	381	501	0.50	396	506	0.59
CH ₂ Cl ₂	358	464	0.87	380	508	0.83	398	511	0.84
EtCOMe	367	480	0.99	382	512	0.29	398	517	0.30
CH ₃ CN	368	490	0.98	381	521	0.22	396	523	0.24
DMSO	369	494	1.00	381	531	0.17	407	538	0.25

Absorption (abs) and emission (em) maxima are reported in nm.

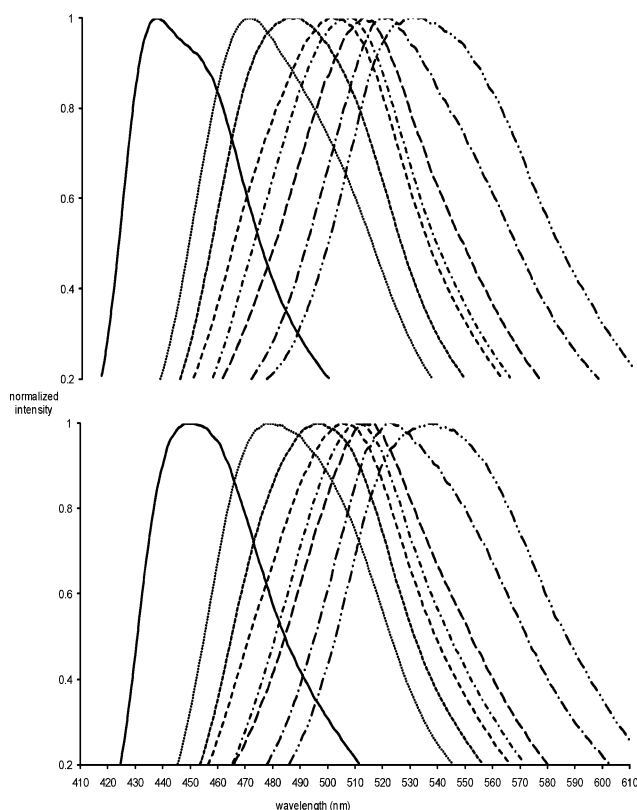


Fig. 2 Normalized emission for **2** (top) and **3** (bottom) in various solvents (—, cyclohexane; ···, toluene; ---, chlorobenzene; - · -, ethyl acetate; ---, dichloromethane; — — —, 2-butanone; — — —, acetonitrile; — — —, dimethylsulfoxide).

0.16 ± 0.05 , respectively. PRODAN has nearly unit quantum yield in ethanol.

The ground state and excited state dipole moments for **2** and **3** are determined from solvatochromism data using the Onsager model.¹⁰ In the Lippert-Mataga plot (Fig. 3, primary axes) the Stokes shift ($\tilde{\nu}_a - \tilde{\nu}_e$) is plotted vs. the solvent polarity factor Δf (eqn (1), where $2\pi\epsilon_0\hbar c = 1.105 \times 10^{-35} \text{ C}^2$).¹¹ In the Mataga plot (Fig. 3, secondary axes) the emission maximum ($\tilde{\nu}_e$) is plotted vs. a slightly different solvent polarity factor (eqn (2)).¹² The Mataga equation is valid when the absorption band does not shift significantly – as is the case here. The solvents used in these plots range in polarity from toluene to dimethyl sulfoxide. No polar protic solvents were used because they significantly

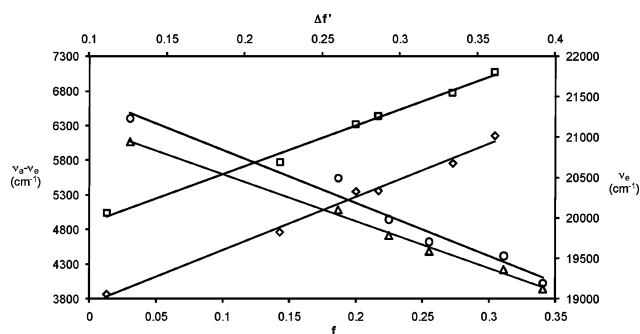


Fig. 3 Lippert-Mataga (positive slope) and Mataga (negative slope) plots for **2** (□, ○) and **3** (◇, Δ).

quench the fluorescence of **2** and **3**. For example, the fluorescence of **2** in methanol is two orders of magnitude smaller than in toluene. While H-bonding has a significant effect on PRODAN's solvatochromism,^{13–17} it hardly affects the emission intensity.

$$\tilde{\nu}_a - \tilde{\nu}_e = \frac{2}{4\pi\epsilon_0\hbar c a^3} (\mu^* - \mu)^2 \Delta f + \text{const.}, \quad (1)$$

$$\text{where } \Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

$$\tilde{\nu}_e = -\frac{2}{4\pi\epsilon_0\hbar c a^3} \mu^* (\mu^* - \mu) \Delta f' + \text{const.}, \quad (2)$$

$$\text{where } \Delta f' = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{1}{2} \frac{n^2 - 1}{2n^2 + 1}$$

The slopes of the best fit lines along with the appropriate Onsager radii (a) for these compounds are sufficient for calculating μ^* and μ . The Onsager radii (**2**, 4.56 Å; **3**, 4.64 Å) are estimated from the mass-density formula assuming a density of 0.95 g mL⁻¹.¹⁸ It should be noted that the Onsager model assumes that the solute is spherical; nevertheless, the model is routinely applied to planar, oblong aromatic fluorophores like **2** and **3**. Both compounds show nearly identical slopes ($m_{\text{L-M}}$) in the Lippert-Mataga plots: 7000 cm⁻¹ for **2** and 7700 cm⁻¹ for **3**. For PRODAN the slope is 6600 cm⁻¹. In the Mataga plots the slopes ($-m_{\text{M}}$) are -7700 cm⁻¹ and -6800 cm⁻¹, respectively. The dipole moments for the ground and excited states derived from these plots (eqn (3a), (3b) and (4))¹⁰ are shown in Table 2 together with those available from semiempirical calculations (*vide infra*). Eqn (3a) gives a value consistent with the others in the table, whereas eqn (3b) does not. The latter is a result

Table 2 Ground (μ) and excited state (μ^*) dipole moments for **2** and **3**

State	Dipole moment/D			
	From eqn (3)	From eqn (4) using indicated values for μ		
S_1	8.9	10.1	9.8	8.9
S_0	0.8	4.7	4.0	4.7
S_1	9.2	8.8	8.4	8.3
S_0	1.0	4.3	3.4	4.3

of the slopes being very similar in magnitude. The calculation of the ground state dipole moment uses the difference of these values. Eqn (4) is used for cases where the ground and excited state dipole moments are not parallel. For **2** and **3** the in-plane component changes by 20–30°. While the values for μ^* show some variability, the general result is that they are just under 10 D, and the ground state dipole moments are about half of that value. The values for **3** are slightly smaller than those for **2**. By comparison, the ground state dipole moment for PRODAN is around 6 D and doubles to 12 D in the excited state.⁹

$$\mu^* = \sqrt{\frac{2\pi\epsilon_0\hbar c a^3}{m_{L-M}}}(m_M)^2 \quad (a) \quad \mu = \sqrt{\frac{2\pi\epsilon_0\hbar c a^3}{m_{L-M}}}(m_M - m_{L-M})^2 \quad (b) \quad (3)$$

$$\mu^* = \sqrt{\mu^2 + (2m_M - m_{L-M})^2 2\pi\epsilon_0\hbar c a^3} \quad (4)$$

Determination of how solvent affects the emission of these compounds can be made through multiparameter regression analysis. Of the several solvent scales that have been developed, the generalized treatment of Catalán is particularly useful because it separates the non-specific effects into a polarizability term (SP) and a solvent dipolarity term (SdP).¹⁹ The other two terms in this approach are specific interaction effects: a solvent acidity term (SA) and a basicity term (SB). The empirical relationship between the Stokes shift and these solvent factors is expressed by eqn (5). Because only aprotic solvents are used, the SA term is ignored. Results for the regression analysis are shown in Table 3. Two analyses are performed for each compound, one using all three factors and one using just the solvent dipolarity factor. The fit of the Stokes shift data is nearly as good with the single factor as with three factors. The errors associated with either the SP term or the SB are as great or greater than the coefficient. These results suggest that the solvatochromism for **2** and **3** in aprotic solvents is due to simple dipolarity.

$$\tilde{\nu}_{\text{abs}} - \tilde{\nu}_{\text{em}} = c_1\text{SP} + c_2\text{SdP} + c_3\text{SA} + c_4\text{SB} + \tilde{\nu}_0 \quad (5)$$

Computational studies

The electronic structures for the first two singlet roots of **2** and **3** are calculated using the AM1 semiempirical method. The

Table 3 Regression results (cm⁻¹) for eqn (5)

	SP	SdP	SB	Intercept	r^2
2	-740 ± 1040	3240 ± 290 3200 ± 210	-50 ± 450	3510 ± 770 2980 ± 140	0.974 0.971
3	1290 ± 1070	3400 ± 300 3590 ± 240	450 ± 450	2800 ± 800 3770 ± 160	0.978 0.970

advantage to this method is that it allows for large CAS-CI level calculations that incorporate the effect of solvent. The CI level for these calculations is set to 12, and only singly and doubly excited microstates are considered. The value of 12 was chosen by examining the effect of CI level on the microstate composition in PRODAN. The composition varies as the CI level is increased, but it remains relatively constant for CI levels of 10 and higher. The characteristics for the ground, Franck–Condon (vertical) and relaxed excited states for **2** and **3** are shown in Table 4. While there is some degree of configuration interaction in all of the excited states, the primary microstate is one with a singly occupied HOMO and LUMO. The relaxed excited state configuration has a higher percentage of this microstate. By analogy with naphthalene, this transition is along the short-axis and labeled as ¹L_b using the Platt classification. The excited states for **2** and **3** have higher dipole moments than the respective ground states. When the excited states relax to their lowest energy structures, the dipole moments increase further. Unlike the case with PRODAN, neither compound has another close-lying excited electronic state. In fact, the nearest singlet state is at least 0.60 eV higher in energy. As a result, neither compound is predicted to undergo internal conversion to an ICT state with a different electronic configuration as is the case with PRODAN.^{20,21}

To determine the optimal dihedral angle of the carbonyl group, the heats of formation for the ground and first excited states are calculated for a series of increasing twist angles. The plots of energy vs. twist angle are shown in Fig. 4. The calculations suggest that the carbonyl group in the six-membered ring structure is not quite coplanar with the naphthalene ring due to the steric interaction with the peri-hydrogen. While the tendency for planarity increases

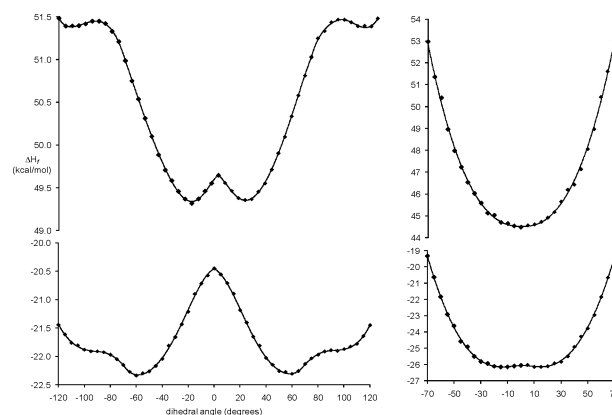


Fig. 4 Calculated ΔH_f (kcal mol⁻¹) in toluene for **2** (left) and **3** (right) for the ground state (bottom) and the first singlet excited state (top) as a function of dihedral angle between the carbonyl group and the naphthalene ring.

Table 4 Calculated ground and excited-state configurations for **2** and **3**

	Solvent	State	Half-occupied orbitals in S ₁ microstates (%)					μ/D	Energy/eV
			HO/LU	HO/LU+1	HO-1/LU	HO-1/LU+1	HO-1/LU+2		
2	toluene	S ₀						4.0	0
		S ₁ (FC)	56.0	10.9	5.4	11.7	0.8	7.2	3.253
		S ₁ (relaxed)	63.2	6.9	4.0	8.7	0.6	7.9	2.947
	CH ₃ CN	S ₀						4.7	0
		S ₁ (FC)	59.1	9.2	4.0	11.0	0.8	8.1	3.095
		S ₁ (relaxed)	66.3	5.4	2.8	7.8	0.7	8.9	2.747
3	toluene	S ₀						3.4	0
		S ₁ (FC)	42.5	16.3	10.3	12.2	0.9	4.6	3.263
		S ₁ (relaxed)	57.7	9.2	5.4	9.8	0.5	6.6	3.095
	CH ₃ CN	S ₀						4.3	0
		S ₁ (FC)	47.5	13.7	7.9	12.3	1.3	5.5	3.177
		S ₁ (relaxed)	64.3	6.2	3.2	8.1	0.6	8.3	2.719

in the excited state, the potential energy surface is very flat. Deviations by 30° only increase the potential energy by 1 kcal mol⁻¹. On the other hand, the propionyl group is predicted to be significantly twisted (~60°). In the excited state the twisting is reduced to 20°. Again, there is very little barrier to further twisting out-of-plane. By way of contrast, the carbonyl group in PRODAN is predicted to be planar, and the increase in potential energy for twisting is much steeper.² The potential energy surface for twisting in **2** bears a striking similarity to the PRODAN derivative where the carbonyl group is part of a seven-membered ring.² These compounds have in common the unusual quenching behavior with protic solvents. Indeed, twisting about the carbonyl group appears to provide an efficient deactivation channel in protic solvents.

Conclusions

Compounds **2** and **3** bearing a carbonyl group in the 5-position on the naphthalene ring have been prepared and their photophysical behavior has been characterized and compared with that of PRODAN. These compounds are slightly less efficient fluorophores than PRODAN. Their solvatochromic behavior is very similar to that of PRODAN; however, all of the bands are red-shifted relative to PRODAN because the first excited state is lower energy. The emissive state for both is ¹L_b, and it has inherent charge transfer character. Unlike the case with PRODAN, there is no close-lying excited state that would allow for formation of a distinct ICT state. These results may help in interpreting the complex behavior of PRODAN. In particular, they suggest that the initially formed excited state of PRODAN has some charge transfer character, but that the ultimately formed ICT state has significantly more, especially in polar and polar protic solvents.

Experimental

General methods

NMR spectra were recorded on a Varian Mercury 400-Vx system. High resolution ESI-MS were acquired with a Bruker Apex-Qe instrument. Fluorescence emission data were collected using a SLM-Aminco SPF-500 spectrometer as the excitation source and the Ocean Optics system as the detector. Solvents used for photophysical characterization were spectrophotometric grade

from Acros. Relative quantum yields in toluene were determined using anthracene ($\Phi = 0.30$), 9,10-diphenylanthracene ($\Phi = 0.90$) and 9,10-dibromoanthracene ($\Phi = 0.094$) as references using the method of standard additions. AM1/SM5C semiempirical calculations were performed using AMPAC 9.0 from Semichem, Inc. Calculations incorporated the following keywords: AM1; SDCI = 12; singlet; qscf; sm5c; solvnt = 'solvent'; tight; truste; micros = 0; root = 1 (or 2); scfct = 0.

Bromonaphthalenes **4**^{2,5} and **5**⁶ were available from previous studies and were sublimed under vacuum prior to use.

1-(6-(Dimethylamino)naphthalen-1-yl)propan-1-one

Bromonaphthalene **4** (1.35 g, 5.4 mmol) was dissolved in dry THF (40 mL), and the mixture was cooled to -78 °C under Ar. BuLi (3.6 mL, 1.6 M in hexanes, 5.8 mmol) was added slowly dropwise, and the reaction was stirred for 30 min. A solution of *N*-propionylpyrrole⁶ (700 mg, 5.68 mmol) in THF (5 mL) was added slowly dropwise. The reaction was stirred and allowed to warm to -40 °C over 1.5 h. The reaction was quenched by pouring into water (300 mL), and the aqueous mixture was stirred overnight. The next day NaCl (30 g) and acetic acid (30 mL) were added. The resulting solution was extracted with ether (2 × 100 mL), and the combined ether layers were washed with water (2 × 50 mL) and 2% aq. NaHCO₃ (3 × 50 mL). The organic layer was dried over Na₂SO₄, and the solvent was removed *in vacuo*. The residue was purified by liquid chromatography using a gradient elution with hexanes and ethyl acetate (*R*_f 0.64, 25% EtOAc/hexanes) giving **2** (700 mg, 3.1 mmol, 57%) after vacuum (0.1 Torr) sublimation. Mp 77–78 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.47 (d, *J* = 9.4 Hz, 1H, Ar-H), 7.78 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.58 (d, *J* = 7.3 Hz, 1H, Ar-H), 7.43 (dd, *J* = 8.1, 7.3 Hz, 1H, Ar-H), 7.23 (dd, *J* = 9.4, 2.5 Hz, 1H, Ar-H), 6.91 (d, *J* = 2.5 Hz, 1H, Ar-H), 3.05 (m, 8H, CH₂-CH₃ and N-CH₃), 1.26 (t, *J* = 7.3 Hz, 3H, CH₂-CH₃); ¹³C NMR (CDCl₃) δ 205.73, 148.69, 135.95, 135.86, 130.94, 126.87, 124.89, 123.84, 123.30, 117.97, 106.66, 40.79, 35.26, 8.96. UV (toluene) λ (log ϵ) 381 nm (3.41). HRMS (ESI): calcd. for C₁₅H₁₇NONa⁺ [M+Na]⁺ 250.12024; found 250.12027.

7-(Dimethylamino)-2,3-dihydrophenanthren-4(1H)-one

Zinc dust was sifted successively through 60, 100, and 200 mesh sieves. It was washed successively with 1 N HCl (3×), H₂O (2×),

EtOH (1×), and Et₂O (1×), then dried *in vacuo* overnight. This zinc (2.0 g, 31 mmol) was slurried in dry dimethylacetamide (20 mL) and activated with I₂ (250 mg, 1 mmol) under Ar. When the red color of I₂ had dissipated, Br(CH₂)₃CO₂CH₃ (4.0 g, 22 mmol) was added. The slurry was heated to 80 °C for 3 h, then cooled to RT. Bromonaphthalene **5** (1.97 g, 7.9 mmol) and Ni(PPh)₃Cl₂ (250 mg, 0.38 mmol) were added. The reaction was stirred under Ar at for 1 h. The mixture was poured into pet. ether (400 mL), and the organic layer was washed with ice-cold water (4 × 25 mL). The organic layer was concentrated *in vacuo*. This residue (1.5 g) was covered with polyphosphoric acid (~5 mL), and the mixture was heated to 110 °C for 45 min. The reaction was cooled and water (100 mL) was added. The solution was neutralized with NaHCO₃, and the precipitate was collected with suction and washed with H₂O. After air-drying, the solid was sublimed under vacuum (0.1 Torr) giving **3** (1.18 g, 4.94 mmol, 62% over 2 steps) as a yellow solid. Mp 86–90 °C; ¹H NMR (400 MHz, CDCl₃): δ 9.28 (d, *J* = 9.5 Hz, 1H, Ar–H), 7.73 (d, *J* = 8.5 Hz, 1H, Ar–H), 7.25 (dd, *J* = 9.5, 2.7 Hz, 1H, Ar–H), 7.18 (d, *J* = 8.5, 1H, Ar–H), 6.86 (d, *J* = 2.7 Hz, 1H, Ar–H), 3.02 (m, 8H, CH₂–CH₂–CH₂ and N–CH₃), 2.73 (t, *J* = 6.6 Hz, 2H, CH₂–CH₂–CH₃), 2.14 (tt, *J* = 6.6, 6.2 Hz, 2H, CH₂–CH₂–CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 201.10, 148.34, 143.21, 134.78, 133.12, 127.70, 127.45, 127.27, 124.24, 118.62, 107.12, 41.41, 40.81, 31.52, 23.47. UV (toluene) λ (log ε) 395 nm (3.33). HRMS (ESI): calcd. for C₁₆H₁₇NONa⁺ [M+Na]⁺ 262.12024; found 262.11979.

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