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# A 2,6-Diformylnaphthalene-1,8:4,5-bis(dicarboximide): Synthesis and Knoevenagel Condensation with Malononitrile

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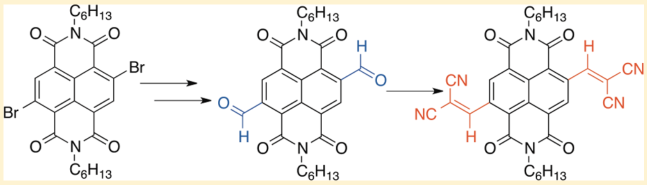
Supporting Information

**ABSTRACT:** Ozonolysis of the 2,6-divinyl derivative of a naphthalene diimide (NDI) affords a 2,6-diformyl-NDI, which can be used in Knoevenagel condensation reactions, as demonstrated by the synthesis of a 2,6-bis(2,2-dicyanovinyl)-NDI. UV−vis absorption and electrochemical data are compared to those of the parent NDI.

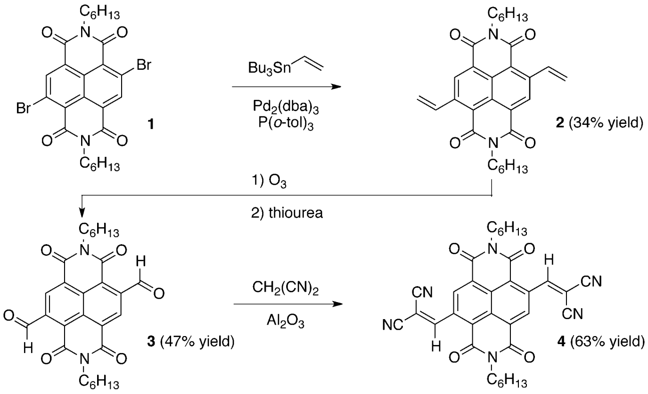


Naphthalene-1,8:4,5-bis(dicarboximide)s (NDIs) are of interest in research fields including electron and energy transfer, organic photovoltaic devices,[1] n-channel organic field-effect transistors,[1] dye lasers,[2] optical switches,[3] and photodetectors,[4] and as G-quadruplex ligands.[5] The optical and electrochemical properties of NDIs can be tuned by variation of the substituents in the 2,6-core positions; those introduced to date include halo, amino, mecapto, alkoxy,[6,7] cyano,[8,9] and cyano-functionalized dithiine and dithiolylidene.[10,11] Moreover, incorporation of NDIs into larger $\pi$-conjugated molecules or into conjugated polymers also relies on the availability of appropriately substituted NDI reagents; to date most species with extended conjugation, including aryl,[9,12] heteroaryl,[12−15] and alkynyl-substituted derivatives,[9] have been obtained from palladium-catalyzed coupling with 2-bromo or 2,6-dibromo NDIs, although recently we have reported 2-stannyl and 2,6-distannyl NDIs and their use in synthesizing oligo-NDIs,[16] 2,6-diacyl-NDIs,[17] and extended NDI/perylene diimide fused systems.[18]

Aldehydes can be useful in synthesizing extended conjugated systems using Knoevenagel, Wittig, and Horner−Emmons reactions; however, to date, formyl NDI derivatives have not been reported. Here we report the synthesis of a 2,6-diformyl-NDI derivative and its conversion to the corresponding 2,6-bis(2,2-dicyanovinyl) derivative, along with optical and electrochemical characterization of these compounds.

The electron-poor nature of NDIs mean that neither the Vilsmeier formylation nor bromine−lithium exchange followed by treatment with reagents such as DMF are likely to be applicable: the Vilsmeier reaction generally fails for electron-poor substrates,[19] while alkyl and aryllithiums are both powerful one-electron reductants[20] and capable of acting as nucleophiles toward imides.[21,22] Accordingly, we turned to the ozonolysis of alkene derivatives. As shown in Scheme 1, *N,N*′-di(*n*-hexyl)-2,6-dibromonaphthalene-1,8:4,5-bis(dicarboximide),[14] **1**, was converted by Stille coupling[23] with tri-*n*-butyl(vinyl)stannane to *N,N*′-di(*n*-hexyl)-2,6-divinylnaphthalene-1,8:4,5-bis(dicarboximide), **2**, in 34% yield using

**Scheme 1. Preparation of NDI Derivatives 2−4**



$Pd_2(dba)_3$ and $P(o\text{-tol})_3$ as the catalyst system. The dialdehyde, **3**, was obtained from **2** by treatment with ozone in 1,1,2,2-tetrachloroethane at −20 °C, followed by addition of thiourea. As an example of the use of **3** in obtaining more extended conjugated systems, **3** was converted to *N,N*′-di(*n*-hexyl)-2,6-bis(2,2-dicyanovinyl)naphthalene-1,8:4,5-bis(dicarboximide), **4**, via a Knoevenagel condensation with malononitrile in toluene in the presence of basic $Al_2O_3$;[24] **4** was isolated in 63% yield. These compounds were characterized by $^1H$ and $^{13}C\{^1H\}$ NMR spectroscopy, high-resolution mass spectrometry, and elemental analysis.

The optical and electrochemical properties of **3** and **4** were compared to those of the corresponding parent NDI, *N,N*′-di(*n*-hexyl)naphthalene-1,4:5,8-bis(dicarboximide). The UV−vis absorption spectra of **2**−**4** in dichloromethane are shown in Figure 1, and their maxima are summarized in Table 1. The divinyl species, **2**, shows a vibronically structured absorption with a very similar maximum to that of the unsubstituted NDI with the addition of another band at somewhat lower energy.

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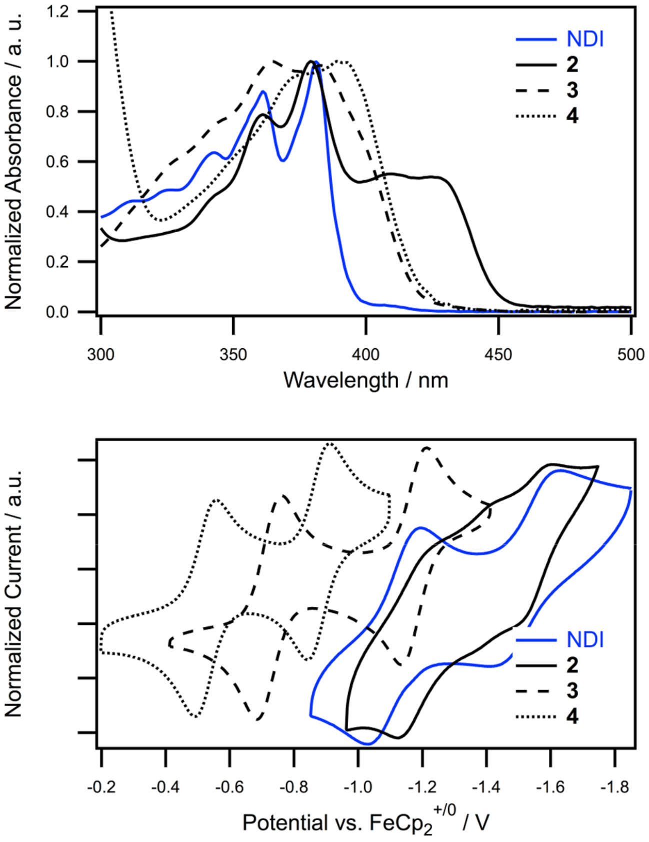

**Figure 1.** UV−vis spectra in $CH_2Cl_2$ (top) and cyclic voltammograms in $CH_2Cl_2$/$^n$$Bu_4NPF_6$ (bottom) of NDI and compounds **2**−**4**.

**Table 1. Optical[a] and Electrochemical[b] Properties of NDI and 2−4**

| compd | $\lambda_{max}$/nm | $E_{1/2}^{0/-}$/V | $E_{1/2}^{-/2-}$/V |
|---|---|---|---|
| NDI | 361, 380 | −1.11 | −1.53 |
| **2** | 361, 380, 405, 420 | −1.17[c] | −1.52[c] |
| **3** | 364, 382 | −0.72 | −1.17 |
| **4** | 376, 389 | −0.53 | −0.89 |

[a] $CH_2Cl_2$. [b] 0.1 M $^n$$Bu_4NPF_6$/$CH_2Cl_2$ vs $FeCp_2^{+/0}$. [c] Irreversible.[25]

Although the dialdehyde, **3**, shows a similar maximum to NDI, it also exhibits a prominent low-energy shoulder and less well-resolved vibronic structure than NDI; this may be contrasted to the spectra of diacyl NDIs,[17] which much more closely resemble that of NDI. The malononitrile adduct shows an absorption maximum red-shifted by ca. 1100 $cm^{-1}$ relative to that of NDI and a somewhat different band shape. Overall, these observations suggest some mixing between the $\pi$-orbitals of the CH═X (X = $CH_2$, O, $C(CN)_2$) moieties and those of the NDI core, whereas the greater steric bulk of the acyl groups leads to a greater twisting between the core and substituent $\pi$-systems and, hence, to primarily inductive effects on the core.

Cyclic voltammetry for **3** and **4** showed two reversible reduction waves corresponding to the sequential reduction of each NDI to the radical anion and dianion (Table 1, Figure 1). The electrochemistry for **2** was less strightforward and less reversible, consistent with the presence of terminal vinyl groups.[25] The dialdehyde, **3**, is significantly more readily reduced than analogous diketones (the dihexanoyl derivative is reduced at −0.90 V versus $FeCp_2^{+/0}$, Cp = $\eta^5$-cyclopentadienyl)[17] despite the similar electron-withdrawing properties of formyl and simple acyl substituents.[26] This observation is consistent with less twist between the substituent and core $\pi$-system in the formyl case, as also suggested above in the context of comparing the optical properties of **3** and the diketone derivatives. Although **4** is more easily reduced than **3**, consistent with the expected effects of the dicyanovinyl group, it is still less readily reduced than 2,6-dicyano-NDIs (−0.40 V vs $FeCp_2^{+/0}$),[8] despite the similar electron-withdrawing properties of CH═$C(CN)_2$ and CN (as quantified by Hammett and field substituent constants[26]). This is likely due to the dicyanovinyl group being noncoplanar with the NDI core due to steric effects (although, as noted above, it is likely less distorted from coplanarity than acyl substituents).

To conclude, we have developed a straightforward synthesis of 2,6-diformyl derivatives of NDI. The activity of the diformyl derivative in Knoevenagel condensation reactions was demonstrated by the synthesis of a 2,6-bis(dicyanovinyl)-NDI. Optical and electrochemical data suggest some $\pi$-orbital interactions between the core and the substituents but that these interactions are likely limited by steric effects. Diformyl-NDIs may be useful building blocks for new core-substituted small-molecule and polymeric NDIs.

## ■ EXPERIMENTAL SECTION

**General Experimental Methods.** Starting materials were reagent grade and were used without further purification unless otherwise indicated. *N,N′*-Di(*n*-hexyl)-2,6-dibromonaphthalene-1,4,5,8-bis-(dicarboximide), **1**, was synthesized according to the literature procedure.[16] Toluene was dried by passing through columns of activated alumina. All reactions were performed using oven-dried glassware under a nitrogen atmosphere unless otherwise specified. Chromatographic separations were performed using standard flash column chromatography methods. Electrochemical measurements were carried out under nitrogen in dry deoxygenated 0.1 M tetra-*n*-butylammonium hexafluorophosphate in dichloromethane using a conventional three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and a Ag wire coated with AgCl as the pseudoreference electrode. Potentials were referenced to $FeCp_2^{+/0}$ by using ferrocene as an internal reference. Cyclic voltammograms were recorded at a scan rate of 50 mV $s^{-1}$. UV−vis−NIR spectra were recorded in 1 cm cells in dichloromethane solvents. Melting point values ($T_m$) were determined using differential scanning calorimetry at a scan rate of 5 °C $min^{-1}$ (the temperature range reported corresponds to the width of the melting transition peak, and the value in parentheses corresponds to the peak of the transition). High-resolution mass spectrometry (HRMS) was performed using an electron ionization (EI) source on a forward geometry, three sector tandem mass spectrometer equipped with a gas chromatograph.

*N,N′-Di(n-hexyl)-2,6-divinylnaphthalene-1,8:4,5-bis-(dicarboximide),* **2.** A solution of **1** (2.00 g, 3.38 mmol), tri(*n*-butyl)vinyltin (2.25 g, 7.09 mmol), tris(dibenzylideneacetone)-dipalladium (0.309 g, 0.338 mmol), and tri(*o*-tolyl)phosphine (0.411 g, 1.35 mmol) in dry toluene (35 mL) was heated to 100 °C for 1.5 h. After cooling, the reaction mixture was filtered through a plug of Celite, eluting with dichloromethane; the filtrate was then concentrated via rotary evaporation, and the crude product was purified by flash chromatography (silica gel, 1:1 dichloromethane/hexanes, $R_f$ = 0.4). The product was recrystallized from isopropanol and collected as a yellow-orange solid (0.552 g, 1.13 mmol, 34%, $T_m$ = 167−176 (171) °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.81 (s, 2H), 8.12 (dd, *J* = 17.7, 11.1 Hz, 2H), 6.03 (dd, *J* = 17.7, 0.6 Hz, 2H), 5.76 (dd, *J* = 11.1, 0.6 Hz, 2H), 4.13 (t, *J* = 7.6 Hz, 4H), 1.70 (quint., *J* = 7.7 Hz, 4H), 1.48−1.22 (m, 12H), 0.87 (t, *J* = 7.1 Hz, 6H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) $\delta$ 163.4, 162.4, 143.2, 135.8, 132.1, 126.9, 125.7, 121.8, 121.1, 41.1, 31.5, 27.9, 26.8, 22.5, 14.0. HRMS (EI) *m/z* calcd for $C_{30}H_{34}N_2O_4$ ($M^+$), 486.2519; found, 486.2522. Anal. Calcd for

$C_{30}H_{34}N_2O_4$: C, 74.05; H, 7.04; N, 5.76. Found: C, 73.90; H, 6.93; N, 5.74.

*N,N′-Di(n-hexyl)-2,6-diformylnaphthalene-1,8:4,5-bis(dicarboximide),* ***3.*** A solution of **2** (1.05 g, 2.16 mmol) in dry 1,1,2,2-tetrachloroethane (35 mL) was deoxygenated with $N_2$ and cooled in a dry ice/1,2-dichlorobenzene bath (−20 °C). The $N_2$ inlet was removed and replaced with an $O_3$ input stream. $O_3$ was bubbled through the reaction mixture for 30 min while the reaction was monitored by TLC. Upon completion of the reaction, the $O_3$ inlet was removed and replaced with $N_2$. A solution of thiourea (0.345 g, 4.53 mmol) in methanol (4.4 mL) was added, and the reaction mixture was stirred at −20 °C for 1 h. The flask was removed from the cooling bath and allowed to warm to room temperature. The reaction mixture was washed with saturated aqueous $Na_2CO_3$ and water, dried over $Na_2SO_4$, and filtered through a plug of Celite, eluting with chloroform. The filtrate was concentrated under vacuum, and the crude product was purified by flash chromatography (silica gel, 1% methanol in dichloromethane, $R_f$ = 0.4). The product was precipitated into hexanes and collected as a yellow solid (0.499 g, 0.833 mmol, 47%, $T_m$ = 275−284 (282) °C). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.12 (s, 2H), 9.02 (s, 2H), 4.19 (t, $J$ = 7.7 Hz, 4H), 1.73 (quint., $J$ = 7.6 Hz, 4H), 1.47−1.37 (m, 4H), 1.37−1.24 (m, 8H), 0.88 (t, $J$ = 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) $\delta$ 191.3, 162.8, 161.4, 141.2, 131.1, 128.2, 127.2, 125.7, 41.4, 31.4, 27.9, 26.7, 22.5, 14.0. HRMS (EI) $m/z$ calcd for $C_{28}H_{30}N_2O_6$ ($M^+$), 490.2104; found, 490.2069. Anal. Calcd for $C_{28}H_{30}N_2O_6$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.45; H, 6.24; N, 5.65.

*N,N′-Di(n-hexyl)-2,6-bis(dicyanovinyl)naphthalene-1,8:4,5-bis(dicarboximide),* ***4.*** A solution of **3** (0.025 g, 0.051 mmol), basic $Al_2O_3$ (0.120 g, 1.22 mmol), and malononitrile (0.025 g, 0.408 mmol) in dry toluene (3 mL) was heated to 70 °C overnight. Another portion of malononitrile (0.013 g, 0.204 mmol) and basic $Al_2O_3$ (0.060 g, 0.612 mmol) was added, and the reaction was heated for 3 h while being monitored by TLC. Upon completion, the toluene solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica gel, 10% ethyl acetate in chloroform, $R_f$ = 0.5) to yield a shiny yellow solid (0.019 g, 0.032 mmol, 63%, $T_m$ = 183−194 (190) °C). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.94 (s, 2H), 8.88 (s, 2H), 4.16 (t, $J$ = 7.8 Hz, 4H), 1.80−1.64 (m, 4H), 1.50−1.28 (m, 12H), 0.90 (t, $J$ = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) $\delta$ 162.3, 161.0, 160.7, 136.3, 132.1, 127.8, 127.1, 124.5, 111.9, 110.8, 90.0, 41.8, 31.4, 27.8, 26.7, 22.5, 14.0. HRMS (EI) $m/z$ calcd for $C_{34}H_{30}N_6O_4$ ($M^+$), 586.2329; found, 586.2318. Anal. Calcd for $C_{34}H_{30}N_6O_4$: C, 69.61; H, 5.15; N, 14.33. Found: C, 69.69; H, 5.07; N, 14.11.

## ■ ASSOCIATED CONTENT

### Supporting Information

NMR spectra of compounds **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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