Synthesis and Physical Characterization of Some New Hydrophobic Forms of the Solvatochromic *N*,*N*-Dialkyl-*p*-nitroanilines

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Introduction

p-Nitroanilines have elicited broad interest and application in the fields of materials and analytical sciences on account of their solvatochromism[1−7] and nonlinear-optical (NLO) properties.[8−13] The relevant structural feature of these chemicals is their "push−pull" π-conjugated electron arrangement. A variety of substituted *p*-nitroanilines act as *solvent-sensitive* (solvatochromic) indicators. The solvent-dependent shifts of their UV/vis spectral bands form the basis of several solvent polarity scales.[1−3] Newer, more hydrophobic forms of these indicators are presently being developed as probes of the polarity of solute binding environments and of permeability in micelles, lipid bilayers, and biological membranes.[7,14−15] *p*-*N*itroanilines also exhibit relatively large first-order hyperpolarizabilities (β),[8,10,13] the molecular phenomenon associated with second-harmonic generation (SHG), which refers to the doubling of the frequency of transmitted light. The latter material property is a potentially very useful NLO effect and is highly sought as it can be exploited to create memory storage devices, switches, and radiation-protective coatings.[16]

In this work, we focus on some new long-chain *N*,*N*-dialkyl-*p*-nitroanilines: *N*,*N*-dipentyl-, *N*,*N*-dihexyl-, *N*,*N*-dioctyl-, *N*,*N*-didecyl-, and *N*,*N*-didodecyl-*p*-nitroanilines (Figure 1). Compounds **1c**−**g** (Figure 1) constitute new hydrophobic forms of the solvatochromic π* indicators of solvent dipolarity/polarizability.[1,4] These new dyes also may be useful in furthering our understanding of the potential utility of alkyl chain length as a strategy for designing crystal lattices of *p*-nitroanilines with high SHG activity. The *n*-alkyl-*p*-nitroanilines recently have been investigated in this respect.[13] Some practical approaches for the synthesis of **1a**−**g** as well as a discussion of crystallographic structures of the long-chain (*N*,*N*-didecyl) vs short-chain (*N*,*N*-dipropyl) di-*n*-alkyl dyes are addressed briefly here. A preliminary look at the solvatochromic properties of **1f** and **1g** in comparison to the shorter chain homologues also is given.

Results and Discussion

Synthesis. The traditional method for preparing the lower homologues (C_1−C_4) of the di-*n*-alkyl-*p*-nitroanilines has involved the reaction of *p*-halonitrobenzene (usually the chloro-substituted species) with the appropriate di-*n*-alkylamine.[17−19] Typically, these reactions are carried out under high pressure,[17−19] as the substitution of aromatic halides with bulky secondary and tertiary amines reportedly is difficult to accomplish at ambient pressures.[19−21] While these conditions are severe and the reaction times long, the approach is attractive because the product is achieved in a single step and with few side products and reactions. Other single-step methods such as *n*-alkylation of selected *p*-nitroanilines or direct nitration of the *N*,*N*-dialkylaniline have limitations. In the case of *n*-alkylation, the electron-withdrawing NO_2 moiety reduces the nucleophilicity of the anilino nitrogen, thus diminishing the yield of the desired di-*n*-alkylated product. Direct nitration of the aniline has been shown to be practical in situations where the para-substituted product is crystalline and easily separated from its oil-phase meta isomer.[7] In a previous paper, we nitrated *N*,*N*-dipropylaniline in cooled solutions of $NaNO_3$ and H_2SO_4 and successfully isolated the crystalline *N*,*N*-dipropyl-*p*-nitroaniline.[7] We found that the success of this procedure, however, was directly related to the fact that of all the species in the reaction mixture, only the desired product was crystallized at room temperature. Analysis, via GC−MS, of extracts of the reaction mixture revealed the presence of several nitro- and dinitro-substituted *N*,*N*-dipropylanilines that were not fully characterized.

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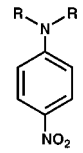

R=	$CH_2CH_2CH_3$	propyl	(a)
	$CH_2(CH_2)_2CH_3$	butyl	(b)
	$CH_2(CH_2)_3CH_3$	pentyl	(c)
	$CH_2(CH_2)_4CH_3$	hexyl	(d)
	$CH_2(CH_2)_6CH_3$	octyl	(e)
	$CH_2(CH_2)_8CH_3$	decyl	(f)
	$CH_2(CH_2)_{10}CH_3$	dodecyl	(g)

Figure 1. *N*,*N*-Dialkyl-*p*-nitroanilines: (a) *N*,*N*-dipropyl-*p*-nitroaniline; (b) *N*,*N*-dibutyl-*p*-nitroaniline; (c) *N*,*N*-dipentyl-*p*-nitroaniline; (d) *N*,*N*-dihexyl-*p*-nitroaniline; (e) *N*,*N*-dioctyl-*p*-nitroaniline; (f) *N*,*N*-didecyl-*p*-nitroaniline; (g) *N*,*N*-didodecyl-*p*-nitroaniline.

The latter approach to nitration would have marginal use in the preparation of longer chain *N*,*N*-dialkyl-*p*-nitroanilines since many of these new dyes (Figure 1, Table 1) are oils at room temperature. Moreover, for the very long chain products (e.g., **1e**−**g**) which *are* crystalline at 25 °C, the reaction would be curtailed by the increasingly limited solubility of the di-*n*-alkylanilines in cold concentrated H_2SO_4. The lack of solvation of the reactants (di-*n*-alkylaniline and nitronium cation NO_2^+) in the same solvent medium would limit their interaction and resulting formation of a product.

In this work, the synthesis of **1a**−**g** was accomplished via nucleophilic substitution at ambient pressures. We found the reaction, which involves 4-fluoronitrobenzene and the corresponding di-*n*-alkylamine (Figure 2), to be useful for the preparation of di-*n*-alkyl-*p*-nitroanilines having a wide range of alkyl chain lengths. Reaction times increased with increasing length of the chains. Increasing the bulkiness of the di-*n*-alkyl moieties negatively affected the reactivity of the species involved.

We note that a series of long-chain *n*-alkyl-*p*-nitroanilines recently was synthesized at ambient pressures via substitution of 4-fluoronitrobenzene (Gangopadhyay et al.[13]). In that work, DMSO was used as the solvent and the reaction times were reported to be 6 h, which is shorter than our reaction times. The primary amines used in that study, however, were less hindered than secondary amines. Moreover, polar aprotic solvents with strong HBA (hydrogen-bond-acceptor) character are more conducive to increasing reaction rates where the nucleophile is a primary amine. The reaction intermediate (produced with a primary alkylamine) has significant HBD (hydrogen-bond-donor) character and is solvated to a greater extent in strong HBA solvents. Reactions reported in this study involving secondary alkylamines benefit less from such a polar aprotic system. The reaction intermediate produced with a secondary alkylamine is bulkier, more nonpolar, and is solvated to a lesser extent in a polar solvent such as DMSO. This phenomenon is especially true with the *N*,*N*-didecyl- and *N*,*N*-didodecyl-*p*-nitroanilines synthesized in this work.

In reacting *N*,*N*-dialkylamines with 4-fluoronitrobenzene, we used a neat system and attempted to drive the reaction by applying an excess of at least 2:1 stoichiometry of the amine to 4-fluoronitrobenzene and by removing HF as the corresponding dialkylamine hydrofluoride salt. Substitution of triethylamine for the second equivalent of the dialkylamine worked equally well (Figure 2). The long-chain di-*n*-alkylamines are slightly more basic than triethylamine,[24] making them a better choice for removing HF. Removal of HF occurred almost exclusively with the use of homogeneously dissolved bases.[25,26]

An advantage of the neat system is that the reaction temperature need not be kept below the boiling point of the solvent. The mechanism in this case is one of base catalysis where previous studies suggest that formation of the product from the intermediate complex is the rate-determining step.[27−31] *N*,*N*-Didodecyl-*p*-nitroaniline, which was the longest chain *N*,*N*-dialkyl-*p*-nitroaniline we examined, formed in 95% yield.

Purification of the oil phase products (**1b**−**d**) was carried out via aqueous acid extraction followed by vacuum distillation and preparative chromatography (TLC or HPLC). In each case, the concentration of strong acid (i.e., HCl or H_2SO_4) in the extraction medium was optimized such that any excess unreacted amine was removed while the product remained in the nonpolar organic layer. This extraction approach exploits the weakly basic nature of *p*-nitroanilines as well as the differing solubilities of the individual dyes (**1b**−**d**) in aqueous solutions of varying HCl or H_2SO_4 concentration. While values of pK_{BH^+} have not been determined for the long-chain products **1c**−**g**, the aqueous-phase basicity of these species should be at least as weak as that of **1b.** The low basicity of the longer alkyl chain species is due, in part, to medium effects where the long alkyl chains on the amine cause steric hindrance to solvation of the protonated form.[7,32−33]

The concentrations of acid in the solutions used to extract contaminants from reaction mixtures containing **1b**, **1c**, and **1d,** respectively, are listed in Table 2. These concentrations show that as the di-*n*-alkyl chains on the product increase in length an increasingly acidic solution can be used to remove contaminants with minimal solubilization of the product. Thus, washing with acid becomes more effective with increasing alkyl chain length because a stronger acid can be used to more effectively extract unwanted components from the organic layer without removal of the product. Creating conditions that minimize solubilization of the *N*,*N*-dialkyl-*p*-nitroaniline (in the acid wash) also limits the extent of acid-catalyzed hydrolysis of the dye and the resulting formation of the contaminant *p*-nitrophenol. The latter species (where formed) was removed in the final chromatography step.[34] It should be noted that washing with acid was not needed for purification of **1e**−**g** since these products were

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Table 1. Some Physical Properties of Nine *N,N*-Dialkyl-*p*-nitroanilines

compd	formula	phase (25° C)	MW (g mol^{-1})	MP (°C)	ref
N,N-dimethyl-*p*-nitroaniline	$C_8H_{10}N_2O_2$	crystal	166	163−165, 159−161	1, 17, 18, 22
N,N-diethyl-*p*-nitroaniline	$C_{10}H_{14}N_2O_2$	crystal	194	77−78, 72−73	1, 17, 18, 23
1a	$C_{12}H_{18}N_2O_2$	crystal	222	62−63, 52−54 57−58	1, 7, 17, this work
1b	$C_{14}H_{22}N_2O_2$	oil	250		1,7, 17, this work
1c	$C_{16}H_{26}N_2O_2$	oil	278		this work
1d	$C_{18}H_{30}N_2O_2$	oil	306		this work
1e	$C_{22}H_{38}N_2O_2$	crystal	362	31	this work
1f	$C_{26}H_{46}N_2O_2$	crystal	418	47−48	this work
1g	$C_{30}H_{54}N_2O_2$	crystal	474	55−56	this work

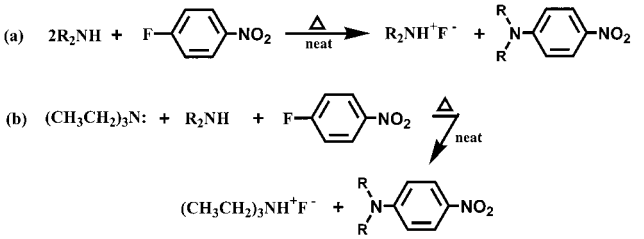

Figure 2. Reaction of 4-fluoronitrobenzene with a long-chain dialkylamine (a) or with dialkylamine plus the triethylamine proton scavenger (b) to produce the *N,N*-dialkyl-*p*-nitroaniline.

Table 2. Concentrations of H_2SO_4 and HCl (M) Used in the Workup of the Oil-Phase Products 1b−d

product	H_2SO_4	HCl
1b	3.5	7
1c	4.6	9.2
1d	5	10

crystallized directly from the organic solution. A summary of general physical properties for nine *N,N*-dialkyl-*p*-nitroanilines including the new compounds prepared here is given in Table 1.

X-ray Crystallography of 1a and 1f. Of the seven *N,N*-dialkyl-*p*-nitroanilines synthesized in this work (Figure 1, Table 1), **1a** and **1e−g** formed crystalline products. The compounds with intermediate alkyl chain length **1b−d** formed oils at room temperature, which is not surprising considering the absence of functional groups capable of forming hydrogen bonds. X-ray diffraction data were collected on single crystals of **1a** and **1f** and the crystal structures solved to characterize molecular structure unambiguously and to examine how an increase in the length of the alkyl chains affects crystal packing.

The molecular structures of **1a** and **1f** in the solid state are shown in Figure 3 and in an ORTEP drawing that is included with the available X-ray crystallographic data (Supporting Information). The nitro groups on **1a** and **1f** are not coplanar with the benzene ring, but instead twist out of the mean plane of the ring by 3° and 10°, respectively. The di-*n*-alkyl groups on **1a** and **1f** also are not coplanar with the benzene ring. The plane defined by the nitrogen atom and the two bonded carbon atoms of the alkyl groups is twisted out of the mean plane of the ring by 5° and 7°, respectively, in **1a** and **1f**. The anilino nitrogen atom appears to be fully sp^2-hybridized in both structures. The carbons in the propyl chains of **1a** all reside in the anti-staggered conformation, as expected. All but two of the carbons in the decyl chains of **1f** reside in the anti-staggered conformation as well. The fourth and fifth carbon atoms in this chain adopt a Gauche conformation that gives a torsion angle of 68°. This conformation causes the decyl chains to bend in the middle so that the ends of the chains align with the long axis of the molecule. The molecules in **1a** and **1f** pack by forming layers of molecules (Figure 3a,b) that build up

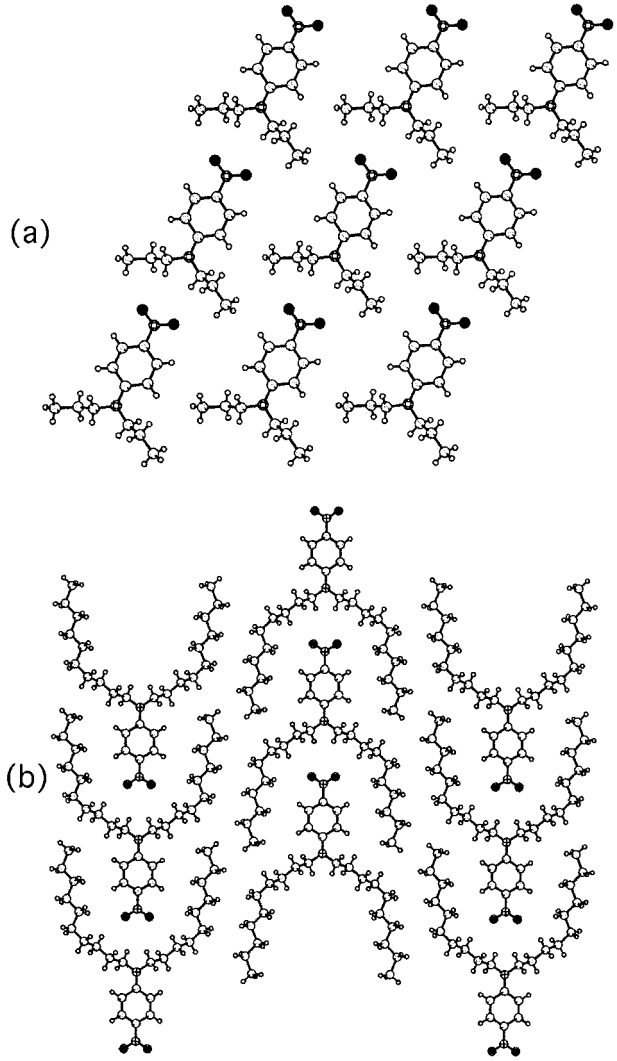

Figure 3. Views of molecular packing within a single layer of the compounds **1a** (a) and **1f** (b).

the crystal by stacking. A feature common to both structures is that the molecules align in a head-to-tail arrangement that forms chains. Analysis of intermolecular contacts shows that the oxygen atoms on the nitro groups in both structures form short C−H···O interactions (**1a**, H···O = 2.59 Å, C···O = 3.32 Å, C−H···O = 133.2°; **1f**, H···O = 2.52 Å, C···O = 3.41 Å, C−H···O = 151.1°) with the third carbon atom in the alkyl chains of the di-*n*-alkyl groups. These contacts are less than the sum of the van der Waals radii of oxygen (1.52 Å)[35] and hydrogen (1.20 Å).[35] Taylor and Kennard have established that C−H···O interactions form commonly in organic crystals when nitro groups are present.[36] Desiraju has demonstrated that C−H···O interactions frequently direct the assembly of molecules into chains and other

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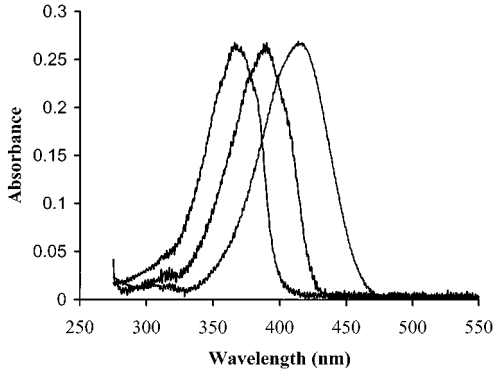

Figure 4. UV/vis spectra of **1g** in cyclohexane (left spectrum), benzene (middle spectrum), and DMSO (right spectrum): υ_{max} =27.26 (kK or 10^3 cm^{-1}) for cyclohexane, 25.82 for benzene, and 24.20 for DMSO (see ref 44).

supramolecular motifs during crystallization in the absence of more traditional strong O−H···O and N−H···O hydrogen-bonding interactions.[37] In the case of **1a** and **1f**, it is likely that the C−H···O interactions are the primary organizational force responsible for directing the molecules to assemble into chains. In the absence of additional hydrogen-bonding interactions, control over the alignment and orientation of the chains within the layers is most likely determined by maximizing van der Waals contacts between alkyl groups at the periphery of the chains. The chains can be oriented either in a parallel or an antiparallel fashion. For example, the chains are oriented in a parallel arrangement in **1a** such that the molecules are all oriented in the same direction within a given layer. One consequence of this arrangement is that the layers in **1a** lack a center of symmetry and are polar. This polarity is preserved during the stacking of the layers to form a bulk crystal that also is polar. Since bulk polarity of a crystal is one of the requirements for second-harmonic generation, crystals of **1a** may show NLO behavior. The chains in **1f** are oriented in an antiparallel arrangement, which gives layers that contain a center of symmetry and that are nonpolar.

Solvatochromic Properties. The new dyes (**1f**,**g**) also were investigated with respect to their performance as solvent-sensitive indicators. A chief goal with regard to this property has been to obtain a homologous series of π^* indicators[1,2,7] whose solvatochromic properties are very similar but whose hydrophobic surface binding properties vary. Such a series of indicators would allow the specific polarity-related properties of a wider variety of solute binding environments in micelles and lipid bilayers to be probed. Indicators with di-*n*-alkyl-*p*-nitroaniline structure have been found to be useful for this effort.[14,38−41]

Some UV/vis spectral shifting properties of *N*,*N*-didodecyl-*p*-nitroaniline (**1g**) are illustrated in Figure 4. The individual spectra of **1g** in cyclohexane, benzene, and DMSO are shown. Estimates of ϵ at λ_{max} obtained previously for other new dyes in the series, in cyclohexane and DMSO, have shown ϵ to be relatively high (e.g., 21000−25000 L mol^{-1} cm^{-1}) and independent of increasing length of the alkyl chains.[14,42] Cyclohexane and DMSO are the reference solvents for the π^* scale of solvent dipolarity/polarizability developed by Kamlet, Abboud, and Taft, where $\pi^* = 0.00$ for cyclohexane and 1.00 for DMSO.[1,2] The π^* value for benzene has been reported to be 0.59.[1] Values of solvent π^* are normalized transition energies calculated from the frequencies of maximum absorption obtained from the spectra of one (or another) indicator in the solvents of interest.[1−2,43] The magnitude of spectral shift over a range of known solvent polarities (e.g., π^*) determines the extent to which a particular indicator can resolve small differences in polarity associated with different solvation environments. In designing indicators to probe micelles and bilayers, such capability is important.

UV/vis spectra of **1g** (Figure 4) and **1f** (not shown) in cyclohexane and DMSO show shifts in peak maxima (between these two reference solvents) of 46.0 and 46.4 nm, respectively. These spectral positions and shifts are consistent with those obtained for other shorter chain *N*,*N*-dialkyl-*p*-nitroanilines in the series whose solvatochromic properties have been previously characterized.[44] The *N*,*N*-dialkyl-*p*-nitroanilines are known to be more strongly solvatochromic than other π^* indicators.[1,44] Now, there is the added benefit of having a series of these particular nitroanilines (Figure 1) in which there is similarity in solvatochromic behavior across a range of homologues. Such similarity will allow direct comparisons to be made among the spectral data and polarity parameters obtained from these different dyes. A rigorous relative measure of the spectral shifting capability[44] of the new π^* indicators is currently underway.

Experimental Section

^{1}H NMR spectra were measured at 200 and 500 MHz on Varian FT-NMR instrumentation. Chemical shifts were referenced to tetramethylsilane (TMS). $CDCl_3$ was used as the supporting solvent (in all NMR measurements). Melting points were obtained via the capillary tube method using a Hoover melting point apparatus. All separations were carried out using thin-layer chromatography (TLC) and gas chromatography with mass spectrometric detection (GC/MS). Diagnostic TLC was performed using Whatman 250 μm silica gel plates. GC/MS data were collected on an HP Model 5890 chromatograph with an HP Model 5971 mass selective detector. Molecular weights were taken from the mass spectral data. Preparative liquid chromatography was carried out using a Varian Dynamax SD-300 HPLC system with UV/vis detector and a 41.1 mm × 250 mm C_{18} (reversed-phase) column (8 μm particles with 100 Å pores). Elemental analysis of the final products was obtained from

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(42) In a previous study,[14] plots of A at λ_{max} vs concentration (M) were carried out for **1e** and **1f** in cyclohexane and DMSO for several estimated values of λ_{max}. The purpose of the study was to demonstrate the lack of a concentration dependence in λ_{max}. The study showed that values of ϵ for the two dyes (estimated from the slopes of the linear plots) were within each other's margin of error. Estimates of ϵ (at λ_{max}) for **1e** and **1f** in cyclohexane were 21 000 and 21 500 (L mol^{-1} cm^{-1}), respectively. For DMSO, the values were 24 500 and 23 100 (L mol^{-1} cm^{-1}), respectively. An uncalibrated 1 cm path length cuvette was used for these measurements.
(43) Kamlet, M. J.; Abboud, J. L.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.
(44) The relative (solvent-dependent) spectral shifting capability of an individual π^* indicator (i.e., indicator of solvent dipolarity/polarizability)[1,2] can be expressed as $-s$, from the linear solvation energy relationship (LSER) $\upsilon_{max} = \upsilon° + s\pi^*$, where υ_{max}= the frequency of maximum absorption of the dye in a solvent of interest (in 10^3 cm^{-1}), $\upsilon°$ = the frequency of maximum absorption of the dye in cyclohexane, π^* is the unitless polarity parameter, s = the slope of the linear plot of υ_{max} vs π,* expressing the change in experimental υ_{max} over a range of known π^*.[1,2]

Huffman Laboratories (Golden, CO). All commercially obtained reagents were used without further purification.

General Procedure for Synthesis. Compounds **1a**−**g** were prepared and isolated using the following general procedure. The procedure is illustrated using **1a** as an example. Modifications to the purification step for the oil phase **1b**−**d** and to the reaction and purification steps for synthesis and isolation of the longer chain (crystalline) **1f**,**g** are given in parentheses and in the following sections.

An excess of di-*n*-propylamine, 8.035 g (0.0796 mol), was mixed with 5.5081 g (0.0391 mol) of 4-fluoronitrobenzene and heated at a gentle boil for 1−3 days (longer reaction times are required for the longer alkyl chain amines). These reactions could be carried out using ground glass reaction vessels. However, we found that the yield was not much changed when the reactions occurred in open glassware, such as in a 100 mL Erlenmeyer flask. The completion of the reactions was monitored by TLC.

After the mixture was cooled to room temperature, approximately 35 mL of diethyl ether (dry reagent) was added (50 mL for the synthesis of **1e**, **1f**, and **1g**). The mixture was warmed lightly until all the solid was dissolved. The flask was stoppered, and the solution was left to allow slow crystallization. Fifteen milliliters of hexane was added (40 mL for the synthesis of **1e**, **1f**, and **1g**), and the white crystals of *N*,*N*-dipropylamine hydrofluoride precipitated. The amine hydrofluoride salts were removed by vacuum filtration and rinsed with cold hexane, and the wash was combined with the filtrate. The solvents were removed (from the combined filtrate) under reduced pressure and the residue taken up in hot methanol and transferred to a crystallizing flask, stoppered, and cooled on ice. Scratching of the flask wall was required to initiate crystallization of the product. Crystals of the yellow *N*,*N*-dipropyl-*p*-nitroaniline were rinsed in cold methanol and recrystallized once from methanol.

Procedure for Isolation of 1b−**d.** Following removal of the di-*n*-alkylamine hydrofluoride (see general procedure), the remaining solution was cooled on ice in a stoppered flask and then transferred to a separatory funnel. Initially, all solutions were washed with 100 mL of 3 M HCl. The acid layer was washed with 50 mL of diethyl ether. The combined ether extracts were saved. The ether extract was then washed with 100 mL of a second solution of H_2SO_4 (or HCl) and then again with 5% $NaHCO_3$. The concentrations of acid in the second solution (for successive syntheses) are given in Table 2. The ether extract was dried over anhydrous $CaCl_2$ and filtered. The ether was removed under reduced pressure. The residue was taken up in 40 mL of hot methanol and transferred to a crystallizing flask. The flask was stoppered and placed on ice. The oil was allowed to settle and coalesce, and the overlying solution was decanted and drawn off. The oil was dissolved into another 40 mL of hot methanol. The flask was stoppered and placed on ice. Again, the orange oil was allowed to settle and the supernatant solution was decanted and drawn off. This procedure was repeated one more time. The orange oil was dried by heating under N_2. Afterward, the oil was purified by preparative normal-phase (SiO_2) TLC using toluene as the mobile phase. Alternatively, we were able to purify the compounds by preparative reversed-phase (C_{18} on SiO_2) HPLC using a gradient elution mobile phase (solvent A = 0.1 M aqueous trifluoroacetic acid; solvent B = 0.1 M trifluoroacetic acid in 90/10 CH_3CN/H_2O). The fractions were neutralized with $NaHCO_3$ and extracted into chloroform. The chloroform was removed under reduced pressure. Vacuum distillation proved difficult for the higher molecular weight oils and led to decomposition of a large amount of the product.

Modifications for 1e−**g.** Synthesis of **1e**−**g** followed the general reaction for **1a**. However, equal molar quantities of the dialkylamine and 4-fluoronitrobenzene were mixed, along with an additional molar quantity of triethylamine. For these reactions, crystals of the triethylamine hydrofluoride were isolated by addition of cold hexane (see general procedure for **1a**). Following removal of the crystalline triethylamine hydrofluoride, the solvent was removed under reduced pressure from the remaining solution, and the residue was taken up in hot methanol and transferred to a crystallizing flask. The supersaturated solution required seed crystals and/or scratching of the flask wall to initiate crystallization of the product. Crystallization took place at a reduced ambient temperature of ≤19 °C. The yellow product crystals were filtered and rinsed with cold methanol. The product was recrystallized twice from methanol and again rinsed with cold methanol.

***N*,*N*-Dipropyl-*p*-nitroaniline (1a):** yield 8.51 g (98%); mp 55−56 °C; ^{1}H NMR ($CDCl_3$) δ 0.93 (t 6H, CH_3), 1.64 (h 4H, CH_2), 3.32 (t 4H, CH_2), 6.80 (d 2H, Ar), 8.22 (d 2H, Ar); GCMS *m*/*z* 222, calcd *m*/*z* for $C_{12}H_{18}N_2O_2$ 222. Anal. Calcd for $C_{12}H_{18}N_2O_2$: C, 64.82; H, 8.17; N, 12.60; O, 14.41. Found: C, 64.83; H, 8.35; N, 12.52; O, 14.30.

***N*,*N*-Dibutyl-*p*-nitroaniline (1b).** An 11.05 g (0.0857 mol) portion of dibutylamine was mixed with 6.02 g (0.0427 mol) of 4-fluoronitrobenzene: yield 7.48 g (70%); ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 6H, CH_3), 1.6 (m, 8H, CH_2), 3.34 (t, 4H, CH_2), 6.53 (d, 2H, ArH), 8.07 (d, 2H, ArH); GCMS *m*/*z* 250, calcd. *m*/*z* for $C_{14}H_{22}N_2O_2$ 250; TLC R_f 0.7 (toluene). Anal. Calcd for $C_{14}H_{22}N_2O_2$: C, 67.15; H, 8.86; N, 11.9; O, 12.79. Found: C, 67.18; H, 9.25; N, 11.00; O, 12.57.

***N*,*N*-Dipentyl-*p*-nitroaniline (1c).** A 7.331 g (0.0467 mol) portion of dipentylamine was mixed with 3.290 g (0.0234 mol) of 4-fluoronitrobenzene: yield 6.49 g (56%); ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 6H, CH_3), 1.32 (m, 8H, CH_2 γ to N), 1.61 (p, 4H, CH_2 β to N), 3.32 (t, 4H, CH_2 α to N), 6.51 (d, 2H, ArH), 8.02 (d, 2H, ArH); GCMS *m*/*z* 278, calcd *m*/*z* for $C_{16}H_{26}N_2O_2$ 278; TLC R_f 0.74 (toluene).

***N*,*N*-Dihexyl-*p*-nitroaniline (1d).** A 8.114 g (0.0438 mol) portion of dihexylamine was mixed with 3.035 g (0.0215 mol) of 4-fluoronitrobenzene: yield 3.045 g (46%); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 6H, CH_3), 1.30 (m, 12 H, CH_2 γ, δ and ϵ to N), 1.58 (p, 4H, CH_2 β to N), 3.32 (t, 4H, CH_2 α to N), 6.50 (d, 2H, ArH), 8.05 (d, 2H, ArH); GCMS *m*/*z* 306, calcd *m*/*z* for $C_{18}H_{30}N_2O_2$ 306; TLC R_f 0.76 (toluene); n_D 1.5939/23 °C.

***N*,*N*-Dioctyl-*p*-nitroaniline (1e).** A 12.834 g (0.0532 mol) portion of dioctylamine was mixed with 5.379 g (0.0532 mol) of triethylamine and 7.500 g (0.0532 mol) of 4-fluoronitrobenzene: yield 17.92 g (93%); mp 31 °C; ^{1}H NMR ($CDCl_3$) δ 0.875 (t, 6H, CH_3), 1.295 (m, 20H, CH_2), 1.596 (p, 4H, CH_2), 3.332 (t, 4H, CH_2), 6.52 (d, 2H, ArH), 8.07 (d, 2H, ArH); GCMS *m*/*z* 362, calcd *m*/*z* for $C_{20}H_{34}N_2O_2$ 362; TLC R_f 0.84 (toluene). Anal. Calcd for $C_{22}H_{38}N_2O_2$: C, 72.87; H, 10.57; N, 7.73; O, 8.83. Found: C, 73.15; H, 10.57; N, 7.60; O, 8.68.

***N*,*N*-Didecyl-*p*-nitroaniline (1f).** A 15.817 g (0.0532 mol) portion of didecylamine was mixed with 5.379 g (0.0532 mol) of triethylamine and 7.500 g (0.0532 mol) of 4-fluoronitrobenzene: yield 21.820 g (98%); mp 48−50 °C; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 6H, CH_3), 1.64 (m, 32H, CH_2) 3.32 (t, 4H), CH_2), 6.80 (d, 2H, ArH), 8.22 (d, 2H, ArH); TLC R_f 0.87 (toluene). Anal. Calcd for $C_{26}H_{46}N_2O_2$: C, 74.58; H, 11.08; N, 6.69; O, 7.65. Found: C, 74.57; H, 11.08; N, 6.70; O,7.65.

***N*,*N*-Didodecyl-*p*-nitroaniline (1g).** An 18.799 g (0.0532 mol) portion of didodecylamine was mixed with 5.379 g (0.0532 mol) of triethylamine and 7.500 g (0.0532 mol) of 4-fluoronitrobenzene: yield 23.99 g (95%); mp 56−57 °C; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 6H, CH_3), 1.64 (m, 40H, CH_2), 3.32 (t, 4H, CH_2), 6.80 (d, 2H, ArH), 8.22 (d, 2H, ArH); TLC R_f 0.90 (toluene). Anal. Calcd for $C_{30}H_{52}N_2O_2$: C, 76.20; H, 11.10; N, 5.93; O, 6.77. Found: C, 75.92; H, 11.12; N, 6.05; O,6.91.

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Supporting Information Available: X-ray crystallographic data are given in Tables S1−S10 and in CIF files for compounds **1a** and **1f**. ORTEP drawings showing the molecular structures of **1a** and **1f** also are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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