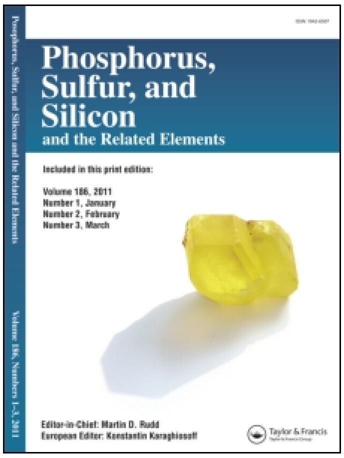

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SYNTHESIS AND CHARACTERIZATION OF TERMINALLY FUNCTIONALIZED n-ALKANETHIOLS

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SYNTHESIS AND CHARACTERIZATION OF TERMINALLY FUNCTIONALIZED n-ALKANETHIOLS

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Syntheses and characterization of a series of terminally functionalized n-alkanethiols with the general formula X-$(CH_2)_n$-SH are reported, where X=OH, NO_2, CO_2H, CO_2Me, CO_2Et, p-NO_2-Ph, p-NH_2-Ph, and n has a value between 5 and 12. These compounds are prepared for the synthesis of self-assembled monolayers on gold surfaces, which provides a simple approach to chemically modified surfaces with controlled interfacial structures.

Keywords: Long-chain alkane thiols; self-assembled monolayers; molecular crystals; interfacial crystal growth

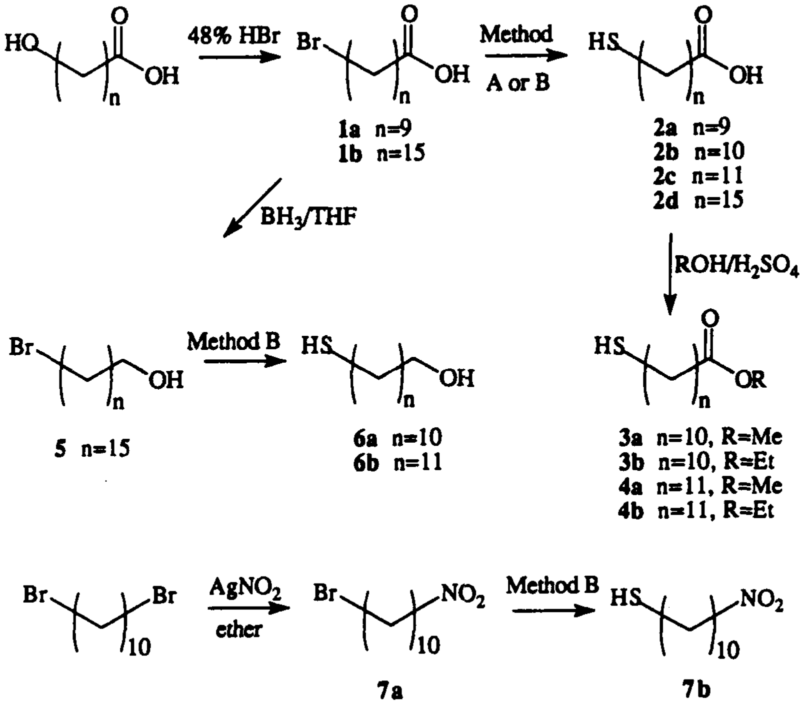
INTRODUCTION

Self-assembly of aliphatic long chain alkanethiols on gold surfaces has been demonstrated to generate immobilized monolayers with controlled surface functionality.[1] This approach promises molecular level control of surface properties that have an impact on numerous important areas of fundamental and technological interest, including electrode modification,[2] protein recognition,[3] nonlinear optical effects,[4] patterning of surfaces,[5] controlled introduction of surface defects,[6] sensors, and controlled wetting.[7] The enormous versatility of organic syntheses provides the opportunity to fabricate interfaces with a diverse variety of chemical functional groups. One objective of our research involves interfacial control of the heterogeneous nucleation and growth of organic molecular crystals. We anticipate that interactions such as hydrogen bonding, charge transfer and van der Waals between self-assembled monolayers and emerging nuclei will play an important role in nucleation and growth rates, crystal morphology and growth orientation.[8] It is also possible that self-assembled monolayers, confined to a non-centrosymmetric surface, may be able to induce formation of non-centrosymmetric crystalline phases, a necessary condition for bulk second-order nonlinear optical effects in organic materials.[9] These studies require examination of the influence of different monolayer functionalities that are capable of designed, specific interactions with the crystalline phases of interest. While numerous reports have appeared that describe the formation of self-assembled organosulfur monolayers, the available chemical functionalities are still rather limited. In addition, detailed synthetic procedures and characterization are rather sparse. This prompted us to develop convenient synthetic procedures for several series of alkanethiols for systematic modification of monolayer properties, including thickness, polarity, hydrogen bonding, charge-transfer and hydrophobicity. We report herein the syntheses and characterization of chemically functionalized mercaptoalkanes that are viable precursors of self-assembled monolayers. These compounds significantly add to the list of reagents available for surface modification, and provide for interfacial molecular functionality that can be exploited in a variety of applications.

RESULTS AND DISCUSSION

The mercaptoalkyl compounds reported herein were designed for the purpose of providing controlled molecular structure at the interfaces of self-assembled monolayers formed by reaction of the terminal sulfhydryl groups with gold surfaces. The synthetic procedures described are general in the sense that they can be employed for any alkane chain length within the specified class of compounds, as defined by the chemical functionality. Therefore, we only report a sufficient number of examples that demonstrate this generality, while describing the synthesis of organosulfur compounds with alkyl chains containing odd and even numbers of carbon atoms that may crystallize differently due to different molecular packing in the solid state. We also report herein the synthesis of some compounds whose use as precursors for self-assembled monolayers has been reported previously, but lacked detailed characterization.[10] The compounds reported provide an opportunity to tailor the surfaces properties in a systematic manner. For example, a polar ester linkage buried beneath the surface at different depths allows systematic tuning of dipole-dipole interactions at the surface. The alkyl chain length and the presence of odd or even number chains is expected to have an impact on the intermolecular packing and order present in self-assembled, monolayers based on these compounds. Whereas hydrogen bonding associated with carboxylic acid functionalities at self-assembled monolayers has been examined, the organosulfur compounds containing amine and nitro functionalities described here provide for hydrogen-bonding interactions at the interface that have not yet been explored. We anticipate that monolayers prepared from these compounds can be particularly useful in sensors that involve specific hydrogen bonding as well as crystal nucleation and growth of nitroanilines, a class of compounds that possess high molecular nonlinear optical hyperpolarizabilities that would be manifested as second harmonic generation (SHG) if non-centrosymmetric phases could be crystallized.[11]

Scheme I shows the general approach used in the preparation of the ω-mercaptoalkanoic acids, their corresponding methyl and ethyl esters, and the

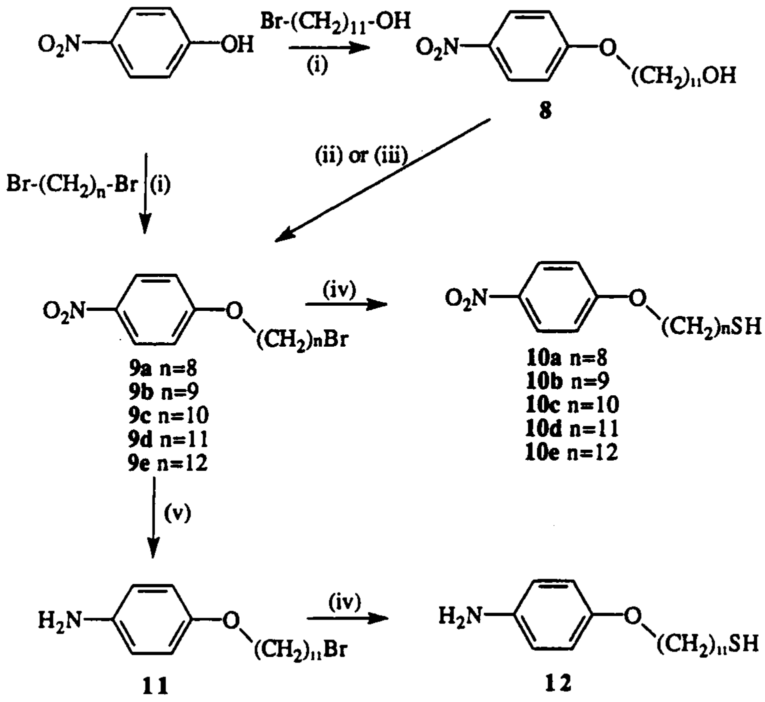


Method A: (i) CH_3COSH/Na; MeOH, Δ
(ii) NaOH/Δ
Method B: (i) $(NH_2)_2C{=}S$; EtOH, Δ
(ii) NaOH/Δ

SCHEME 1

ω-mercaptoalcohols. Bromination reactions used in the preparation of the precursors, ω-bromoalkanoic acids were carried out using hydrobromic acid according to published literature procedures.[12] The bromides were then converted to the thiols by either using thiolacetic acid[13] and sodium metal in methanol,[14] or by using thiourea in ethanol. In both cases, the resulting intermediates were hydrolyzed using sodium hydroxide.[15] Both of these methods gave similar yields of approximately 65–85%, depending on the nature of the bromide. For example, the thiourea route gave a lower yield than the thiolacetic acid route in the synthesis of 11-mercaptoundecanoic acid, **2b**. However, thiourea is generally the preferred conversion reagent because it lacks the offensive odor of thiolacetic acid. In addition, when the bromide contains an aromatic moiety (as is the case for compounds **9, 11**), the thiourea route avoids the possibility of Birch reduction which occurs in the presence of sodium metal.[16] The esters **3** and **4** were prepared from the corresponding acids by using a large excess of the alcohol in the presence of sulfuric acid. 11-Mercaptoundecanol, **6a** was prepared from 11-bromoundecanol using thiourea. Reducing 16-bromo-1-hexadecanoic acid, **1b** (which was synthesized from 16-hydroxyhexadecanoic acid) by using a 1 : 1 borane : tetrahydrofuran complex gave 16-bromohexadecanol **5** as white fluffy crystals which was converted to 16-mercaptohexadecanol, **6b** using thiourea.[17] 1-Mercapto-10-nitrodecane, **7b** was prepared in a two-step synthesis starting from 1,10-dibromodecane. The precursor, 1-bromo-10-nitrodecane, **7a** was obtained as faint yellow crystalline material by stirring a suspension of silver nitrite with an excess of 1,10-dibromodecane in ether at 0°C for 24 hrs in the dark followed by 48 hrs of additional stirring at room temperature.[18] This compound was converted to 1-mercapto-10-nitrodecane using thiourea in 64% yield.

Scheme II shows the general approach used in the synthesis of the nitrophenoxy and aminophenoxy terminated mercaptoalkanes. The use of ω-bromoalcohols gives a clean reaction with nearly quantitative yield of the corresponding ω-(p-nitrophenoxy)alcohols.[19] For example, using 11-bromo-1-undecanol gave compound **8** in 95% yield. Due to the presence of the ether linkage, HBr could not be used in the bromination step, requiring the use of phosphorus tribromide[20] or carbontetrabromide/triphenylphosphine.[21] Because of side reactions, these brominations gave poor to moderate yields (~35–45%) in the conversion of **8** to **9d**. This approach had two drawbacks: the need to synthesize the ω-bromoalcohols, and the several side reactions during the bromination step due to the presence of the long aliphatic chain. An alternative route to these precursors using the commercially available α,ω-dibromoalkanes was attempted. This method proved to be very efficient since it allowed the elimination of one step in the reaction sequence, and gave higher yields of the



(i) Acetone, K_2CO_3/Δ
(ii) PBr_3
(iii) CBr_4/PPh_3
(iv) $(NH_2)_2C{=}S/EtOH$
(v) H_2/Pd

SCHEME II

corresponding terminally disubstituted α-bromo-ω-(p-nitrophenoxy)alkanes. The synthesis of α-bromo-ω-(p-nitrophenoxy)alkanes with long chains ($n > 8$) was accomplished in high yields (50–85%, depending on the reaction times and the nature of the dibromides). Disubstituted products were removed readily because of large solubility differences between these compounds and the corresponding monosubstituted products. For example, the α,ω-bis(p-nitrophenoxy)alkanes crystallized immediately upon cooling hot acetone solutions to room temperature, whereas crystallization of the α-bromo-ω-(p-nitrophenoxy)alkanes required chilling of the remaining acetone solution at 0°C for > 24 hrs. Occasionally these materials do not crystallize even when left in a freezer for long periods of time (up to a week), and addition of a few drops of ethanol, repetitive scratching of the glassware with a spatula, or occasional vigorous shaking is required to initiate crystallization. The extent of disubstitution was minimized by using larger excess of the dibromides (1 : 1.25-1.5), larger solvent volumes, and lower temperatures.

1-(p-Aminophenoxy)-11-mercaptoundecane, **12** was prepared by hydrogenation of the nitro compound **9d** using a modified published procedure that employed 35 psi of hydrogen and Pd on activated carbon in a Parr Pressure Reaction Apparatus with THF as solvent,[22] followed by thiourea conversion of **11** into the desired product, **12**. The synthesis and isolation of the aminophenoxy terminated thiols proved to be difficult. We were able to prepare compound **12** with satisfactory analytical results, but only in a rather low yield (15%).[23]

The experimental section describes the synthesis and characterization of the new organosulfur compounds as well as those that have been reported without synthetic details or characterization. We also report the synthesis of intermediates that have not been previously reported. The disubstituted α,ω-bis(p-nitrophenoxy)alkanes are formed as by-products in the procedure employing α,ω-dibromoalkanes. While these compounds are not directly germane to the synthesis of organosulfur compounds, we have included their syntheses and characterization in the supplementary section in order to enable their identification during synthesis of the desired compounds. To the best of our knowledge, the compounds in this series have not been reported previously, with the exception of the $n = 5$ member.[24] These compounds may serve as precursors for the synthesis of new polymers, including polyimides and epoxy resins. Polyimides with spacer groups of different lengths can provide controlled adhesion and alignment properties, properties that are important in printed circuit board technologies, and liquid crystal flat panel displays.[25]

EXPERIMENTAL

General Comments

Chemicals were obtained from Aldrich and were used without further purification unless stated otherwise. Solvents were reagent grade and were used as received. Melting points were taken on a Mel-Temp II capillary melting point apparatus and are uncorrected. Fourier Transform Infrared (FTIR) spectra were recorded using KBr disks on a Nicolet Magna 550 spectrophotometer. Proton NMR spectra were obtained on a Varian-200 spectrophotometer. Chemical shifts are reported in ppm relative to tetramethylsilane (δ units). Elemental analyses were performed by Galbraith Laboratories Inc. Knoxville, TN. A Parr pressure reaction apparatus was used for the reduction of the nitro compounds to the corresponding amines using Pd on activated carbon in THF and 35 psi of hydrogen gas.

I. Synthesis of ω-mercaptoalkanoic acids; $HS\text{-}(CH_2)_n\text{-}CO_2H$; n = 9, 10, 11, 15

The general synthetic procedure involves the preparation of an ω-bromoacid from the corresponding hydroxy acid by heating at reflux for two days in a 1 : 1 (V : V) mixture of glacial acetic acid and 48% hydrobromic acid. The bromide is then converted to the thiol using one of the following methods. In the first method, the bromide is heated at reflux for 24 hours in thiolacetic acid and sodium metal in methanol (if necessary, ethanol can be used to enhance the bromide solubility), followed by sodium hydroxide hydrolysis of the resulting thioester for an additional 2–4 hours to give the ω-mercaptoalkanoic acid. The second method utilizes an ethanolic solution of thiourea in which the bromide is heated at reflux for 24 hours followed by sodium hydroxide hydrolysis of the resulting intermediate (ω-isothiourea alkanoic acid hydrobromide) to give the ω-mercaptoalkanoic acid. These two methods gave comparable yields (~70%) in most cases. In general, thiourea gives lower yields but practically it is the preferred reagent because it is odorless.

10-mercaptodecanoic acid (2a) 10-Bromodecanoic acid (**1a**) was prepared by heating at reflux a mixture of 10-hydroxydecanoic acid (Aldrich) (5.0 g, 26.6 mmol), 48% hydrobromic acid (50 mL), and glacial acetic acid (50 mL) for 72 hours. Compound **1a** crystallized upon cooling the reaction mixture to room temperature, and was isolated by filtration, washed with water and recrystallized from hexane; 3.78 g (75% yield); mp 32–34°C; H^1 NMR ($CDCl_3$): δ: 3.39 (t.2H), 2.37 (t, 2H), 1.90-1.29 (m, 14H). Anal. Calcd. for $C_{10}H_{19}BrO_2$: C, 47.83; H, 7.57; Br, 31.85. Found: C, 48.06; H, 7.86; Br, 31.55. The thiol was obtained by heating at reflux a mixture of **1a** (2.0 g, 7.97 mmol), thiolacetic acid (1.5 g, 19.6 mmol), and sodium metal (0.4 g, 17.4 mmol) in a 100 mL of methanol. The mixture was gently heated under nitrogen for 24 hours after which time the reaction mixture was allowed to cool to room temperature. Upon cooling the thioester separated as white crystals. A degassed solution (0.8 g, 20.0 mmol) of sodium hydroxide dissolved in 10 mL of deionized water was added to the reaction mixture and heating was resumed for an additional 3 hours under nitrogen. The reaction mixture was then cooled in an ice bath and poured, with stirring, into a 500 mL beaker containing ice-cold water (100 mL), conc. HCl (5 mL) and ether (200 mL). The ethereal layer was separated, washed three times with deionized water (3 × 100 mL) and saturated aqueous NaCl solution (100 mL), and finally washed with 100 mL of deionized water. The ethereal layer was dried over anhydrous Na_2SO_4, filtered, and the ether removed by rotary evaporation. The product, **2a** was obtained as a white waxy material (1.23 g, 61%) H^1 NMR (CDC13): δ 5.32 broad (s, 1H), 3.64 (t, 2H), 2.34 (t, 2H), 1.62 – 1.29 (m, 14H). Anal. Calcd. for $C_{10}H_{20}0_2S$: C, 58.82; H, 9.80; S, 15.69. Found: C, 59.22; H, 9.83; S, 15.50.

11-mercaptoundecanoic acid (2b). **Method A.** 11-Bromoundecanoic acid (7.5 g, 28.3 mmol) was added to a solution containing (4.6 g, 60.0 mmol) thiolacetic acid and (1.5 g, 65.2 mmol) sodium metal in 150 mL of methanol. The reaction was worked up in a similar manner to that described for **2a**. The product was collected as a white powder and then recrystallized from hexane (5.48 g, 73% yield) mp 40–41°C. Anal. Calcd. for $C_{11}H_{22}0_2S$: C, 60.55; H, 10.09; S, 14.68. Found: C, 60.89; H, 10.30; S, 13.84. H^1 NMR spectra: δ 2.45 (t, 2H), 2.36 (t, 2H), 1.60 (p, 4H), 1.30 (m, 12 H).

Method B. 11-Bromoundecanoic acid (7.5g, 28.3 mmol) was added to a solution containing (2.28g, 30.00 mmol) thiourea in 100 mL of ethanol. The mixture was heated at reflux under nitrogen for 24 hours. After cooling to room temperature, the intermediate, 11-isothiourea undecanoic acid hydrobromide began to separate as shiny white crystals. A solution of (1.98 g, 49.5 mmol) sodium hydroxide dissolved in 20 mL of deionized water was added to the reaction mixture, and heating was resumed for additional 5 hours[26]. The reaction mixture was then poured into a 500 mL beaker containing 100 mL of deionized water, 200 mL of ether and 5 mL of conc. hydrochloric acid. The organic layer was then washed twice with deionized water and its volume reduced to about 50 mL. The product, 11-mercaptoundecanoic acid separated as white precipitate upon cooling, and was isolated by filtration and recrystallized from hexane (4.88 g, 65% yield) mp 40–41°C, Anal. Calcd. for $C_{11}H_{22}0_2S$: C, 60.55; H, 10.09; S, 14.68. Found: C, 60.26; H, 10.20; S, 13.72. H^1 NMR spectra: δ 2.45 (t, 2H), 2.36 (t, 2H), 1.60 (p, 4H), 1.30 (m, 12 H).

12-mercaptododecanoic acid (2c). 12-Bromododecanoic acid (5.0 g, 18.87 mmol); sodium metal (0.92 g, 40.0 mmol), and thiolacetic acid (3.04 g, 40.0 mmol) were heated at reflux in 150 mL of methanol for 24 hrs. Base hydrolysis of the intermediate, carried out by heating at reflux for 3 hours, gave the title compound (3.64 g, 72% yield) which was extracted by ether and recrystallized from hexane; mp 42–44°C. H^1 NMR ($CDCl_3$): δ 3.66 (s, 1H), 2.64 (t, 2H), 2.31 (t, 2H), 1.46 (m, 18H). Anal. Calcd. $C_{12}H_{24}0_2S$: C, 62.07; H, 10.34; S, 13.79. Found: C, 62.34; H, 10.16; S, 13.74.

16-bromohexadecanoic acid (1b). 16-Hydroxyhexadecanoic acid (10.0g, 36.6 mmol) was dissolved in 75 mL of a 1 : 1 mixture of hydrobromic acid and glacial acetic acid. The mixture was heated at reflux for 2 days. The title compound was obtained as white crystals (8.2 g, 80% yield); mp 69°C. Anal. Calcd. for $C_{16}H_{31}BrO_2$: C, 57.33; H, 9.26; Br, 23.86. Found: C, 57.41; H, 9.33; Br, 23.83. H^1 NMR ($CDCl_3$): δ 2.53 (t, 2H), 2.35 (t, 2H), 1.42 (m, 26H).

16-mercaptohexadecanoic acid (2d). 16-Bromohexadecanoic acid **1b** (6.0 g, 17.9 mmol), sodium metal (0.85 g, 36.2 mg-atom), and thiolacetic acid (2.5 mL, 36.2 mmol) were dissolved in methanol (100 mL). Compound **2d** was obtained as white crystalline material, (4.1 g, 68% yield); mp 67–69°C; H^1 NMR ($CDCl_3$): δ 2.53 (q, 2H), 2.35 (t, 2H), 2.31 (t, 2H), 1.46 (m, 24H). Anal. Calcd. for $C_{16}H_{32}O_2S$: C, 66.67; H, 11.11; S, 11.11. Found: C, 66.77; H, 11.14; S, 10.56.

II. Synthesis of ω-mercaptoalkanoic esters; $HS\text{-}(CH_2)_n\text{-}CO_2R$; n = 10, 11; R = Me, Et.

1-methyl-11-mercaptoundecanoate (3a). 11-mercaptoundecanoic acid (1.0 g, 4.6 mmol) was dissolved in methanol (50 mL) to which was added a few drops of concentrated sulfuric acid[27]. The reaction mixture was warmed gently with stirring in a water bath for 2 hours. The solution was then concentrated down to about 15 mL and placed in an ice bath. The resulting shiny silver-like crystals which formed were then filtered off and washed with water and cold methanol (0.6 g, 56% yield). Anal. Calcd. for $C_{12}H_{24}O_2S$: C, 62.07; H, 10.34; S, 13.79. Found: C, 62.26; H, 10.60; S, 13.88. H^1 NMR ($CDCl_3$): δ 3.80 (s, 3H), 2.46 (t, 2H), 2.39 (t, 2H), 1.60 (p, 4H), 1.30 (m, 12H).

1-ethyl-11-mercaptoundecanoate (3b). 11-mercaptoundecanoic acid (1.0 g, 4.6 mmol) was dissolved in ethanol (50 mL) to which was added a few drops of concentrated sulfuric acid, and the reaction mixture was warmed gently in a water bath for 2 hours. The crystals which formed upon chilling the reaction mixture were filtered off and washed with water and cold ethanol (0.74 g, 65% yield). Anal. Calcd. for $C_{13}H_{26}O_2S$: C, 63.41; H, 10.57; S, 13.01. Found: C, 62.98; H, 10.29; S, 13.72. H^1 NMR ($CDCl_3$): δ 4.20 (q, 2H), 2.47 (t, 2H), 2.35 (t, 2H), 1.61 (p, 4H), 1.30 (m, 15H).

1-methyl-12-mercaptododecanoate (4a). 12-mercaptododecanoic acid (1.0 g, 4.3 mmol) was dissolved in methanol (50 mL) to which was added a few drops of concentrated sulfuric acid The product was isolated as mentioned for the esters above, (0.48 g, 48% yield). Anal. Calcd. for $C_{13}H_{26}O_2S$: C, 63.41; H, 10.57; S, 13.01. Found: C, 63.08; H, 10.84; S, 13.53. H^1 NMR ($CDCl_3$): δ 3.81 (s, 3H), 3.66 (s, 1H), 2.64 (t, 2H), 2.31 (t, 2H), 1.46 (m, 18H).

1-ethyl-12-mercaptododecanoate (4b). 12-mercaptododecanoic acid (1.0 g, 4.3 mmol) was dissolved in ethanol (50 mL) to which was added a few drops of concentrated sulfuric acid. The product was isolated as mentioned for the esters above, (0.37 g, 34% yield). Anal. Calcd. for $C_{14}H_{28}O_2S$: C, 64.62; H, 10.77; S, 12.31. Found: C, 64.95; H, 10.92; S, 13.02. H^1 NMR ($CDCl_3$): δ 4.16 (q, 2H), 3.66 (s, 1H), 2.64 (t, 2H), 2.31 (t, 2H), 1.43 (m, 18H).

III. Synthesis of ω-mercaptoalcohols; $HS\text{-}(CH_2)_n\text{-}OH$; n = 11, 16.

16-bromo-1-hexadecanol (5). 16-bromo-1-hexadecanoic acid (2.53 g, 7.55 mmol) was placed in a 250 mL three-neck flask containing 20 mL of dry THF. The mixture was then purged with dry nitrogen and the flask put in an ice bath. A syringe charged with 10 mL of 1 : 1 borane : tetrahydrofuran solution was used for the dropwise addition of this reagent to the reaction mixture over a half-hour period. *The reaction flask must allow an escape for the resulting hydrogen gas as mild bubbling occurred upon the addition of the borane complex.* The reaction mixture was then allowed to warm to room temperature and was stirred for 6 hrs. The two phases that formed upon the addition of 10 mL of saturated K_2CO_3 solution were separated, and the organic layer retained. The aqueous layer was washed with ether twice and the ethereal layers were combined with the original organic layer, and concentrated under reduced pressure to yield a white powder which was crystallized from hexane to yield the title compound (2.08 g, 81%); mp 65.5°C. Anal. Calcd. for $C_{16}H_{33}BrO$: C, 59.83; H, 10.28; Br, 24.90. Found: C, 59.47; H, 10.78; Br, 25.07. H^1 NMR ($CDCl_3$): δ 2.64 (t, 2H), 2.31 (t, 2H), 1.46 (m, 28H).

11-mercapto-1-undecanol (6a). 11-Bromo-1-undecanol (5.0 g, 19.9 mmol) and thiourea (1.52g, 20.0 mmol) were heated at reflux for one day followed by NaOH hydrolysis of the resulting intermediate to yield the title compound (4.06 g, 81.2%) as an off-white powder which melts at 29°C. Anal. Calcd. for $C_{11}H_{24}OS$: C, 64.71; H, 11.76; S, 15.69. Found: C, 64.70; H, 11.70; S, 14.53. H^1 NMR ($CDCl_3$): δ 2.64 (t, 2H), 2.31 (t, 2H), 1.46 (m, 28H).

16-mercapto-1-hexdecanol (6b). 16-Bromo-1-undecanol (2.0 g, 6.2 mmol) and thiourea (0.6g, 7.9 mmol) were heated at reflux for one day followed by NaOH hydrolysis of the resulting intermediate to yield the title compound (1.34g, 67%), Anal. Calcd. for $C_{16}H_{34}OS$: C, 70.07; H, 12.41; S, 11.68. Found: C, 70.39; H, 12.66; S, 12.29. H^1 NMR ($CDCl_3$): δ 2.60 (t, 2H), 2.34 (t, 2H), 1.46 (m, 28H).

IV. Synthesis of α-mercapto-ω-nitroalkanes; $HS-(CH_2)_n-NO_2$; n = 10.

10-bromo-1-nitrodecane (7a). Dibromodecane (10.0 g, 33.3 mmol) was added with vigorous stirring at once to a suspension of silver nitrite (3.0g, 19.4 mmol) in 150 mL of dry ether placed in an ice bath in the dark for 24 hrs. The reaction mixture was then allowed to warm up to room temperature and stirring continued for an additional 48 hours. The remaining undissolved solids (silver salts) were removed by filtration and the ethereal layer concentrated and chilled in an ice bath to give pale yellow crystals that melt at room temperature, (6.4 g, 60% yield). Anal. Calcd. for $C_{10}H_{20}BrNO_2$: C, 45.13; H, 7.52; N, 5.27; Br, 30.05. Found: C, 45.59; H, 7.61; N, 5.29; Br, 30.14. H^1 NMR ($CDCl_3$): δ 2.64 (t, 2H), 2.31 (t, 2H), 1.48 (m, 16H).

10-mercapto-1-nitrodecane (7b). 10-Bromo-1-nitrodecane (1.25g, 4.70 mmol) and thiourea (0.4g, 5.2 mmol) were heated at reflux and worked out in the usual manner to give the title compound as a yellow thick oil (0.8g, 64% yield). Anal. Calcd. for $C_{10}H_{21}NO_2S$: C, 54.79; H, 9.59; N, 6.39; S, 14.61. Found: C, 54.86; H, 9.74; N, 6.24; S, 15.03. H^1 NMR ($CDCl_3$): δ 2.68 (t, 2H), 2.28 (t, 2H), 1.44 (m, 16H).

V. Synthesis of α-mercapto-ω-(p-nitrophenoxy)alkanes; $HS-(CH_2)_n-O-(C_6H_4)-NO_2$

These compounds were prepared by one of the two routes shown in scheme II, by heating 4-nitrophenol and potassium carbonate in acetone with either the bromoalcohol $Br-(CH_2)_n-OH$ (which, if not commercially available, can be prepared by reduction of the acid $Br-(CH_2)_{n-1}-CO_2H$) or the terminally substituted dibromide (i.e $Br-(CH_2)_n-Br$). Using the dibromides proved to be better in the case of long chains (n > 8). Due to the presence of the aromatic ring, all the bromides were converted into the corresponding mercaptans using the thiourea route.

V.I. Synthesis of α-bromo-ω-(p-nitrophenoxy)alkanes; $Br-(CH_2)_n-O-(C_6H_4)-NO_2$

1-bromo-8-(p-nitrophenoxy)octane (9a). 1,8-dibromooctane (25 g, 91.90 mmol) and p-nitrophenol (11.5 g, 82.73 mmol) were dissolved in acetone (250 mL) containing K_2CO_3 (15.00 g). The desired product was collected as white crystals (7.05 g, 26% yield based on p-nitrophenol). Anal. Calcd. for $C_{14}H_{20}BrNO_3$: C, 50.92; H, 6.06; N, 4.24; Br, 24.22. Found: C, 50.89; H, 5.99; N, 4.31; Br, 24.38. H^1 NMR ($CDCl_3$): δ 8.17 (d, 2H), 6.92 (t, 2H), 4.02 (t, 2H), 3.35, (t, 2H), 2.15-1.30 (m, 12H).

1-bromo-9-(p-nitrophenoxy)nonane (9b). 1,9-dibromononane (25.0 g, 87.39 mmol) and p-nitrophenol (11.2 g, 80.57 mmol) were dissolved in acetone (250 mL) containing K_2CO_3 (12.50 g, 90.0 mmol). Product collected (8.2 g, 30% yield), mp 39–41°C. Anal. Calcd. for $C_{15}H_{22}BrNO_3$: C, 52.34; H, 6.39; N, 4.07; Br, 23.23. Found: C, 52.43; H, 6.15; N, 3.85; Br, 23.28. H^1 NMR ($CDCl_3$): δ 8.14 (d, 2H), 6.90 (t, 2H), 4.01 (t, 2H), 3.40, (t, 2H), 1.53 (m, 14H).

1-bromo-10-(p-nitrophenoxy)decane (9c). p-Nitrophenol (5.0 g, 36.0 mmol), 1,10-dibromodecane (12.0 g, 40.0 mmol), and K_2CO_3 (5.2 g, 37.2 mmol) were dissolved in acetone (200 mL), and the reaction mixture was heated for 24 hrs. The product, **9c** was collected as off-white crystals after their formation in the filtrate overnight; (9.15 g, 71% yield): mp 52–54°C. Anal. Calcd. for $C_{16}H_{24}BrNO_3$: C, 53.65; H, 6.71; N, 3.91; Br, 22.32. Found: C, 53.86; H, 6.79; N, 4.02; Br, 22.54. H^1 NMR ($CDCl_3$): δ 8.16 (d, 2H), 6.91 (d, 2H), 4.03 (t, 2H), 3.39, (t, 2H), 1.55 (m, 16H).

1-bromo-11-(p-nitrophenoxy)undecane (9d). This compound was prepared by either of two routes. One route involved the reaction of 11-bromo-1-undecanol (5.0 g, 19.9 mmol) with p-nitrophenol (2.78 g, 20.0 mmol) in acetone in the presence of K_2CO_3 by heating for 24 hrs to give white crystalline 11-(p-nitrophenoxy)-1-undecanol **8**, mp 47°C. Anal. Calcd. for $C_{17}H_{27}NO_4$: C, 66.02; H, 8.73; N, 4.53. Found: C, 65.79; H, 6.96; N, 4.63. Bromination of **8** using phosphorous tribromide or carbontetrabromide/triphenylphosphine gave **9d** in 38% yield and 45% yield, respectively. In both cases, the product was purified on a silica gel column with dichloromethane-ethylacetate (9:1) as the eluent. In the second method, 1,11-dibromoundecane (5.0 g, 15.9 mmol), p-nitrophenol (1.8 g, 12.95 mmol) and K_2CO_3 (1.8 g, 13.0 mmol) were dissolved in 150 mL of acetone. The reaction mixture was heated at reflux for 24 hours. The warm solution yielded an off-white to cream colored solid which was isolated by filtration, washed with water and cold ethanol, and dried. It was identified as the disubstituted product, H^1 NMR ($CDCl_3$): δ 8.17 (d, 4H), 6.92 (d, 4H), 4.03 (t, 4H), 1.63 (m, 18H). The monosubstituted product was collected as an off-white crystalline material which formed in the filtrate overnight, (3.76 g, 75% yield); mp 55–56°C. Anal. Calcd. for $C_{17}H_{26}BrNO_3$: C, 54.85; H, 6.99; N, 3.76; Br, 21.48. Found: C, 54.57; H, 6.96; N, 3.94; Br, 21.66. H^1 NMR ($CDCl_3$): δ 8.16 (d, 2H), 6.91 (t, 2H), 4.03 (t, 2H), 3.39, (t, 2H), 1.55 (m, 18H).

1-bromo-12-(p-nitrophenoxy)dodecane (9e). 1,12-Dibromododecane (5.0 g, 15.24 mmol), K_2CO_3 (1.8 g, 13.0 mmol), and p-nitrophenol (1.75 g, 12.6 mmol) were dissolved in acetone and heated at reflux for 12 hrs. The monosubstituted product was mainly formed and was collected as off-white crystalline material (3.9 g, 78% yield); mp 61–63°C. Anal. Calcd. for $C_{18}H_{28}BrNO_3$: C, 55.97; H, 7.26; N, 3.63; Br, 20.70. Found: C, 55.43; H, 7.43; N, 3.28; Br, 20.92. H^1 NMR ($CDCl_3$): δ 8.18 (d, 2H), 6.93 (t, 2H), 4.02 (t, 2H), 3.39, (t, 2H), 1.49 (m, 20H).

V.II. Synthesis of α-mercapto-ω-nitrophenoxyalkanes; $HS\text{-}(CH_2)_n\text{-}O\text{-}(C_6H_4)\text{-}NO_2$

These compounds were obtained from the corresponding bromo derivatives using thiourea as the thiolating agent with moderate yields (30–58%) depending on the nature of the bromoalkane. In general, better yields were obtained when longer reaction times were employed (2 days). Under comparable reaction conditions, longer chains consistently gave higher yields. We include the detailed procedure for one member in this family 1-mercapto-11-(p-nitrophenoxy)undecane **9d**. Other members were prepared using identical procedures.

1-mercapto-11-(p-nitrophenoxy)undecane(10d). 1-bromo-11-(p-nitrophenoxy)-undecane (5.39 g, 14.5 mmol) and thiourea (2.0 g, 26.30 mmol) were dissolved in absolute ethanol (100 mL) and heated at reflux for 48 hrs. Upon cooling to room temperature a fine precipitate was formed. NaOH (1.46 g, 36.5 mmol) dissolved in deionized water (20 mL) was added to the reaction mixture and the mixture was heated for additional 2 hrs. During this time the colorless clear reaction mixture changed into a clear yellow solution which was cooled to room temperature and then poured into a beaker containing conc. HCl (5 mL), cold deionized water (100 mL) and ether (150 mL). The ether layer was then extracted and washed with deionized water and dried over anhydrous sodium sulfate. Evaporation of the solvent afforded the product as yellow powder. Attempts to crystallize the product from a variety of solvents always gave the noncrystalline powder, m.p. 56°C, (3.15 g, 58% yield). Anal. Calcd. for $C_{17}H_{27}NO_3S$: C, 62.77; H, 8.31; N, 4.31; S, 9.85. Found: C, 62.86; H, 8.51; N, 4.33; S, 9.94. H^1 NMR ($CDCl_3$): δ 8.11 (d, 2H), 6.87 (d, 2H), 3.99 (t, 2H), 2.67-2.41 (m, 2H), 1.80-1.25 (m, 18H).

1-mercapto-8-(p-nitrophenoxy)octane (10a). 1-Bromo-8-(p-nitrophenoxy)-octane (2.5 g, 7.58 mmol) and thiourea (0.9 g, 11.8 mmol) were dissolved in ethanol and heated at reflux for 48 hrs. Using a procedure identical to that used in the synthesis of **10d** gave the title compound, **10a** (0.86 g, 34% yield) as a pale yellow powder, m.p. 38°C,. Anal. Calcd. for $C_{14}H_{21}NO_3S$: C, 59.36; H, 7.42; N, 4.95; S, 11.31. Found: C, 59.68; H, 7.80; N, 5.01; S, 12.03. H^1 NMR ($CDCl_3$): δ 8.11 (d, 2H), 6.87 (d, 2H), 3.99 (t, 2H), 2.64 (t, 2H), 1.74-1.23 (m, 12H).

1-mercapto-9-(p-nitrophenoxy)nonane (10b). 1-Bromo-9-(p-nitrophenoxy)-nonane (1.0 g, 5.58 mmol) and thiourea (0.35 g, 4.58 mmol) were dissolved in ethanol and heated at reflux for 48 hrs. The title compound **10b**, was obtained as yellow powder, m.p. 39.5°C, (0.41 g, 39% yield). Anal. Calcd. for $C_{15}H_{23}NO_3S$: C, 60.61; H, 7.74; N, 4.71; S, 10.77. Found: C, 60.88; H, 7.83; N, 4.73; S, 11.06. H^1 NMR ($CDCl_3$): δ 8.14 (d, 2H), 6.93 (d, 2H), 4.86 (s broad, 1H), 4.04 (t, 2H), 2.66 (t, 2H), 1.66-1.16 (m, 14H).

1-mercapto-10-(p-nitrophenoxy)decane (10c). 1-Bromo-10-(p-nitrophenoxy)-decane (2.0 g, 2.90 mmol) and thiourea (0.53 g, 7.0 mmol) were dissolved in ethanol and heated at reflux for 48 hrs. Compound **9c** was obtained as yellow powder, m.p. 51°C, (1.14 g, 57% yield). Anal. Calcd. for $C_{16}H_{25}NO_3S$: C, 61.74; H, 8.04; N, 4.50; S, 10.29. Found: C, 61.91; H, 7.99; N, 4.61; S, 10.47. H^1 NMR ($CDCl_3$): δ 8.12 (d, 2H), 6.94 (d, 2H), 4.01 (t, 2H), 2.65 (t, 2H), 1.59-1.12 (m, 16H).

1-mercapto-12-(p-nitrophenoxy)dodecane (10e). 1-bromo-12-(p-nitrophenoxy)-dodecane (4.03 g, 10.45 mmol) was dissolved in a warm ethanolic solution containing thiourea (1.0 g, 13.2 mmol). Using a procedure similar to that used in the preparation of **10d** gave **10e** as a yellow solid, m.p. 62°C, (2.2 g, 54% yield). Anal. Calcd. for $C_{18}H_{29}NO_3S$: C, 63.72; H, 8.55; N, 4.13; S, 9.44. Found: C, 63.96; H, 8.82; N, 4.16; S, 10.01. H^1 NMR ($CDCl_3$): δ 8.16 (d, 2H), 6.91 (d, 2H), 4.02 (t, 2H), 2.83 (t, 2H), 1.79-1.03 (m, 20H).

VIII. Synthesis of 1-mercapto-11-(p-aminophenoxy)undecane; HS-$(CH_2)_{11}$-O-(C_6H_4)-NH_2

1-bromo-11-(p-aminophenoxy)undecane (11). 1-bromo-11-(p-nitrophenoxy)-undecane **9d** (5.0 g, 13.4 mmol) was dissolved in dry THF (150 mL) and placed in a parr hydrogenation apparatus. To that was added 0.5 g of 10% Pd on activated carbon (Janssen Chemica). The reaction vessel was flushed with hydrogen three times then pressurized at 35 psi. The mixture was allowed to react with shaking for three days. The insoluble substances were filtered off and the solvent evaporated to give **11** as a brown solid, (3.74 g, 75%), mp 132 (dec.).

1-mercapto-11-(p-aminophenoxy)undecane (12). Thiourea (0.75 g, 9.8 mmol), and 1-bromo-11-(p-aminophenoxy)undecane (2.25 g, 6.58 mmol) were dissolved in 75 mL of ethanol and the reaction mixture was heated for 48 hrs. The product was isolated as a cream colored solid (0.34 g, 15%); mp 115°C (dec.). Anal. Calcd. for $C_{17}H_{29}NOS$: C, 73.12; H, 10.39; N, 5.02; S, 11.47. Found: C, 73.48; H, 10.44; N, 5.13; S 13.04. H^1 NMR ($CDCl_3$): δ 8.16 (d, 2H), 6.91 (t, 2H), 4.03 (t, 2H), 3.62 (s, 2H), 3.12 (t, 2H), 1.90-1.27 (m, 18H).

CONCLUSIONS

Synthesis and characterization of a series of terminally functionalized n-alkanethiols of interest to our molecular recognition and interfacial crystal growth studies have been successfully accomplished. These compounds constitute a unique set that would allow the examination of the role of different types of intermolecular interactions on the self-assembled monolayer surfaces and how they affect their properties as well as the way they influence crystal growth of guest molecules on those surfaces.

Supplementary Materials Available

Table summerizing the analytical and H^1 NMR spectral data for the thiols described in this paper, their precursors and the side products, α,ω-bis(p-nitrophenoxy)alkanes (4 pages). Ordering information is given on any current masthead page.

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