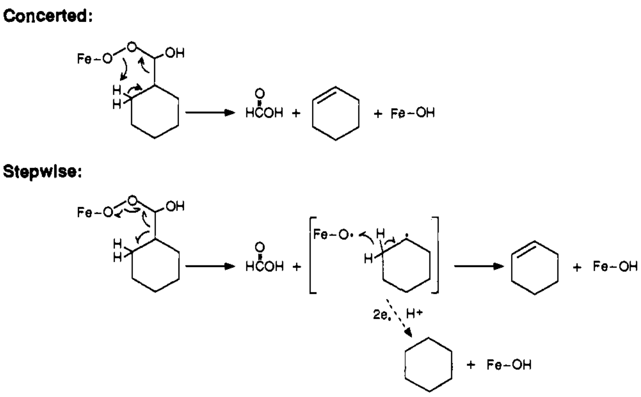
**Scheme I**



only $H_2O_2$ was active. We conclude that "iron oxene" is not the active oxidant in this reaction and propose that a peroxyhemiacetal-like adduct generated from the aldehyde and $O_2$-derived peroxide is a transient enzyme-bound intermediate. Rearrangement of this peroxy intermediate by either a concerted or sequential $\beta$-scission mechanism then yields formic acid and the olefin.

Cyclohexene was identified by gas chromatography/mass spectroscopy in the head-space gas of a reaction mixture containing cyclohexanecarboxaldehyde, NADPH, P-450 $LM_2$,[5,7] reductase,[8] and DLPC. Cyclohexanol, cyclohexyl formate, and cyclohexanecarboxylic acid (which is formed in the reaction) did not yield cyclohexene when substituted for the aldehyde. With substrate labeled with $^{14}C$ at the aldehyde carbon, formate is formed in about an equimolar amount with respect to cyclohexene.

When either of the enzymes or NADPH was omitted, the amount of cyclohexene formed was insignificant (Table I). A small amount of cyclohexane (about 10% of the amount of cyclohexene) was detected with the complete system. At low $O_2$ concentration (4.0 $\mu$M), an 83% decrease in activity was observed, and omission of phospholipid[9] gave a 77% loss. Added catalase and superoxide dismutase had no effect.[10]

Hydrogen peroxide supports the cytochrome P-450 dependent oxidative deformylation of cyclohexanecarboxaldehyde to cyclohexene (Table II). In experiments not shown, formate was found to be produced in the $H_2O_2$-supported reaction in about an equimolar amount with respect to cyclohexene. The inability of iodosobenzene to support the reaction suggests that the generally accepted pentavalent "iron oxene"[4f] is not the oxidant. Furthermore, the results with *m*-chloroperbenzoic acid and cumyl hydroperoxide indicate that deformylation by $H_2O_2$ is mechanistically distinct from hydroxylation reactions supported by these oxidants.[4c-e]

In Scheme I, we propose that an $O_2$-derived, heme iron bound peroxide reacts with the electrophilic aldehyde carbonyl group to form an enzyme-bound peroxyhemiacetal-like intermediate,[3a] rearrangement of which yields the olefin and formic acid by a concerted or a sequential $\beta$-scission mechanism. The small amount of cyclohexane formed is accounted for by reduction of the carbon radical, as in the $\beta$-scission of hydroperoxides to yield alkanes.[11]

In experiments not presented, oxidative deformylation to yield olefins was shown to occur with other cyclic and acyclic aldehydes in the presence of P-450 $LM_2$. Of eight purified P-450 isozymes examined, four were catalytically active in deformylation of cyclohexanecarboxaldehyde to cyclohexene. Oxidative deformylation may be a commonly encountered pathway in the metabolism of xenobiotic aldehydes.

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(5) Abbreviations: P-450 $LM_2$, phenobarbital-inducible rabbit liver microsomal cytochrome P-450, also designated as P-450 IIB4;[6] DLPC, dilauroylglycero-3-phosphocholine; reductase, NADPH-cytochrome P-450 reductase.

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# Substituted $2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''':5'''''',2''''''':5''''''',2'''''''':5'''''''',2''''''''':5''''''''',2''''''''''$-Undecithiophenes: The Longest Characterized Oligothiophenes

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Polythiophenes figure prominently in current research on conducting polymers[1] and are of interest as nonlinear optical materials.[2] In both cases the properties depend critically on the effective conjugation length that can be realized in the polymers, i.e., on their structure and conformation. It is generally assumed that the polymerization of thiophenes leads to regular polymers in which the thiophene units are linked at the $\alpha$-positions.[3] However, little is known about the degree to which deviations from this ideal behavior occurs. For unsubstituted polythiophenes containing seven or more thiophene units, spectral characterization is virtually impossible due to their insolubility.[4] Solubility in regular organic solvents is obtained when polymers derived from 3-alkylthiophenes are prepared.[5] However, adjacent alkyl substituents give rise to steric hindrance and, hence, to a nonplanar conformation.[6] Moreover, the degree of regularity depends

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**Chart I**

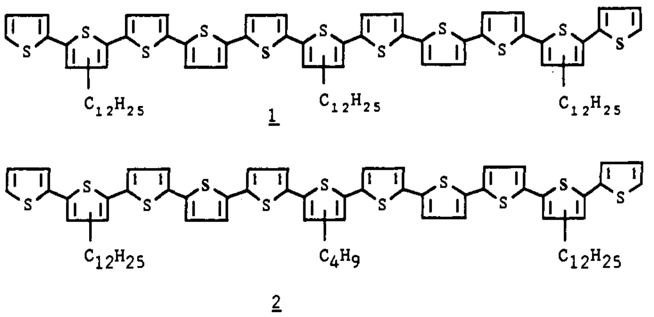


**Table I**

| entry | oligomer[a] | conductivity[b] | $\lambda_{max}$[c] |
|---|---|---|---|
| 1 | T3 d(2) | *d* | 345 |
| 2 | T5 b(2) | 0.01 | 412 |
| 3 | T7 b2(2,6) | 0.20 | 440 |
| 4 | T9 d(4) | *d* | 455 |
| 5 | T11 d2(2,10) b(6) **2** | 20 | 462 |
| 6 | T11 d3(2,6,10) **1** | | 462 |
| 7 | poly(3-hexylthiophene) | 10–100[e] | 430–440[f] |

[a] The short-hand notation used in the table, for example, T11 d2-(2,10) b(6) **2**, for entry 5, reads as follows: 11 thiophene units with two dodecyl groups at units 2 and 10 and one butyl group at unit 6. [b] Specific conductivities (S/cm, four-point method) of thin coherent layers obtained by melting the oligomer on a ceramic plate and doping with iodine at room temperature until saturation. [c] Absorption maximum of a solution in $CHCl_3$. [d] FT-IR and vis absorption spectra after undoping pointed to postpolymerization during doping. [e] Reference 5. [f] Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212.

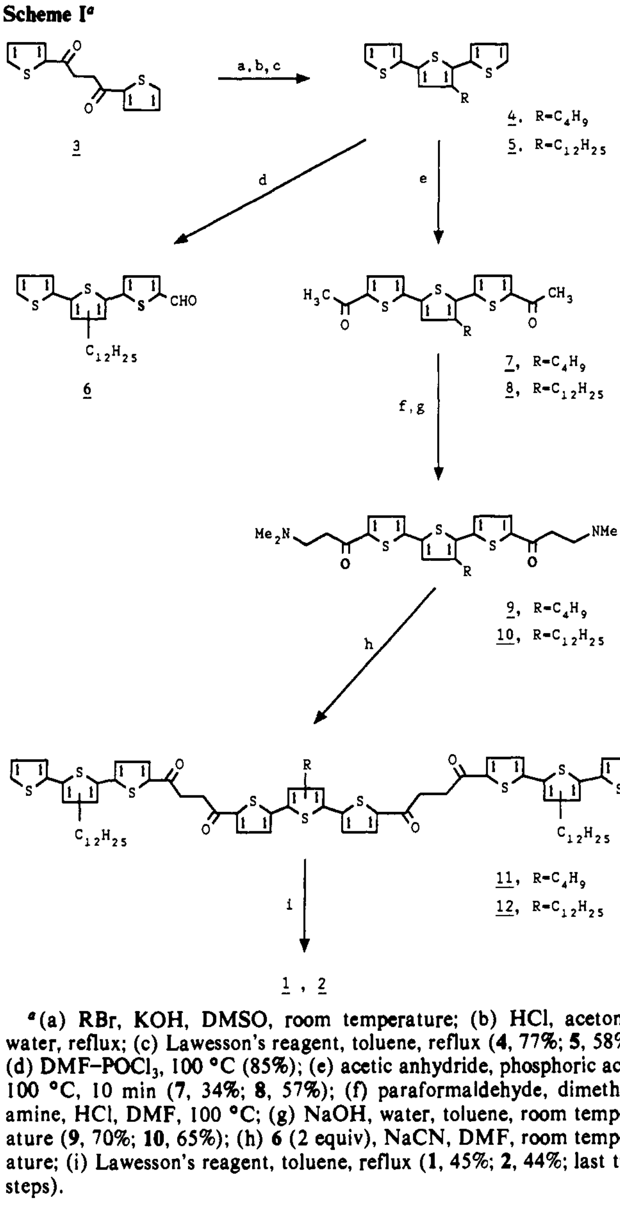
critically on the method of preparation.[7]

We have prepared a number of oligothiophenes carrying a limited number of aliphatic sidechains. The synthetic route leaves no doubt about the ideal all-α,α′ linkage of the thiophene units. This series of soluble oligothiophenes enables use to study the dependence of the conjugation length on the chain length.[8]

As a characteristic example of the synthesis of these oligothiophenes, we report here the preparation of the all-α,α′-linked undecithiophenes **1** and **2**, which at present constitute the longest known all-α,α′-linked oligothiophenes (Chart I).

Diketone **3**[9] (Scheme I) can be conveniently alkylated with 1-bromobutane and 1-bromododecane, using solid KOH in DMSO.[10] Hydrolysis of the crude reaction product, consisting of a mixture of the alkylated diketone and enol ethers, gives the desired alkylated diketones, which are directly transformed into 3′-butylterthiophene **4** or 3′-dodecylterthiophene **5**. Terthiophene **5** is formylated to afford monoaldehyde **6** as a mixture of two isomers (based on $^1H$ NMR and $^{13}C$ NMR). For the middle sections of **1** and **2**, terthiophenes **4** and **5** are converted to the bis-acetylated terthiophenes **7** and **8**. These can then be transformed into the amines **9** and **10**. Subsequently, **9** and **10** are coupled with 2 equiv of aldehyde **6** (Stetter reaction[11]) to give the tetraketones **11** and **12**, both as mixtures of isomers. Finally, a ring closure with Lawesson's reagent leads to the desired undecithiophenes **1** and **2**, as mixtures of isomers. For purification, the undecithiophenes are recrystallized from chlorobenzene after having been filtered over aluminum oxide, hot chlorobenzene being used as the eluent.[12] Using this synthetic strategy, we have synthesized a series of oligothiophenes with different chain lengths and numbers (and sites) of substituents.

**Scheme I**[a]



[a] (a) RBr, KOH, DMSO, room temperature; (b) HCl, acetone–water, reflux; (c) Lawesson's reagent, toluene, reflux (**4**, 77%; **5**, 58%); (d) DMF–$POCl_3$, 100 °C (85%); (e) acetic anhydride, phosphoric acid, 100 °C, 10 min (**7**, 34%; **8**, 57%); (f) paraformaldehyde, dimethylamine, HCl, DMF, 100 °C; (g) NaOH, water, toluene, room temperature (**9**, 70%; **10**, 65%); (h) **6** (2 equiv), NaCN, DMF, room temperature; (i) Lawesson's reagent, toluene, reflux (**1**, 45%; **2**, 44%; last two steps).

The conductivity of iodine-doped oligothiophenes and the optical properties of a selected number of oligomers are given in Table I. The conductivity data of the iodine-doped oligomers increases steadily with chain length. The value for **2**, 20 S/cm, is of the same order of magnitude as that for doped polythiophenes. Hence, the effective conjugation length for doped polythiophenes is not much longer than 11 units. The wavelength of the maximum absorbance of $CHCl_3$ solutions of the oligothiophenes, being a rather direct measure of the conjugation length, increases steadily with chain length and seems to approach saturation (at 11 units) without actually reaching it. The conjugation length of **1** and **2** exceeds that of poly(3-alkylthiophene) (see Table I), due to a decreased steric interaction of side groups which are more widely spaced. Absorption spectra of solid films of both **1** and **2** and

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(12) Elemental analysis for **1** and **2** (calculated values within parentheses). **1** (mp 140–142 °C): C, 67.91 (68.13); H, 6.89 (6.86); S, 24.77 (25.01). **2** (mp 150–161 °C): C, 66.26 (66.62); H, 6.23 (6.21); S, 26.74 (27.17). Due to the low solubility of **1** and **2** in organic solvents (insoluble in DMSO at room temperature; the solubility in hot chlorobenzene is about 1 g/50 mL), we were unable to obtain suitable NMR spectra (DMSO-$d_6$, 100 °C). IR (KBr) for **1**: 3065 (w), 2956 (m), 2924 (s), 2853 (m), 1640 (w, br), 1492 (m), 1460 (m, br), 1261 (m), 1100–1030 (m, br), 870 (m), 832 (m), 804 (s), 788 (s), 687 (m). The IR spectrum of **2** is virtually identical with the spectrum of **1**.

poly(3-alkylthiophenes), however, are much alike, with maxima at higher wavelength (520 nm), indicating a much larger conjugation length in the solid state.[8b] Recently, the third-order nonlinear optical susceptibilities of some of the oligomers have been measured in poled PMMA solutions, and in this case saturation sets in at 7–8 thiophene units, thus indicating the sensitivity of planarity of these oligomers to matrix composition.[8a]

Comprehensive studies on the properties of these undecithiophenes and lower homologues as well as a full account of the synthesis of all these oligothiophenes will be published elsewhere.[8,13]

In conclusion, two oligothiophenes of unprecedented length have been prepared through a solid route. Moreover, these undecithiophenes bridge the gap that exists between the well-characterized lower oligothiophenes (up to sexithiophene) and the vaguely characterized polythiophenes.

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(13) Ten Hoeve, W.; Wynberg, H., to be published.

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## Aluminum and Gallium Oxide Pillared $MoO_3$

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It has been shown that microporous or zeolite-like structures can be constructed by intercalating large clusters between the layers of two-dimensional structures. These "pillaring" reactions were first reported for aluminosilicate clays.[1] They have not been extended to many simple transition-metal oxide hosts, other than titanium,[2] due to the difficulty in opening up the layers sufficiently to allow introduction of a large guest species. There is obvious interest in this approach as a route to developing and/or modifying metal oxides with specific properties. $MoO_3$, in particular, is a multifunctional material which has attracted considerable attention as a partial methane oxidation catalyst[3] and as a potentially viable cathode in secondary batteries.[4] The search for other polytypes of the layered structure of $\alpha$-$MoO_3$ has led to two new phases,[5,6] but neither are microporous. We report here the first examples of pillaring of $\alpha$-$MoO_3$ by the incorporation of $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ ("$Al_{13}$") to give rise to a microporous molybdenum oxide with a high surface area. The layers have also been pillared with a new oxy–gallium cluster which is analogous to the $Al_{13}$ oligomer. Remarkably well-ordered materials are obtained which enables the first direct determination of the orientation of the guest $Al_{13}$ cluster by 1-D Fourier analysis.

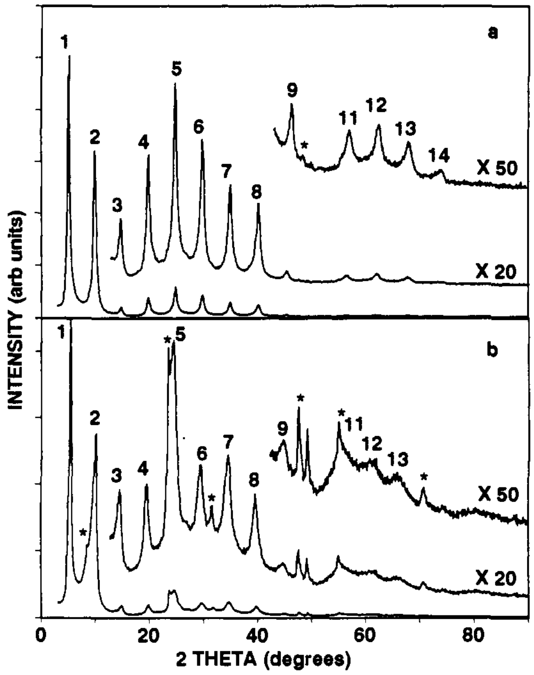

**Figure 1.** X-ray diffraction pattern (Cu Ka radiation) of oriented films of (a) $[(Al_{13})_{0.047}(Na)_{0.003}]MoO_3$ and (b) the 18-Å phase of gallium-pillared $MoO_3$ "$[(Ga_{13})_{0.032}(Na)_{0.09}]MoO_3$". Reflections arising from residual $[Na(H_2O)_2]_{0.25}MoO_3$ ($d_{0k0}$ = 11.39 Å)[7] are marked with an (*). The intensity has been expanded by a factor of 20 and 50 in the upper traces in the figures; the integers indicate the (0*k*0) indices.

We prepared our pillared compounds by combining a solution of the guest cation species with a dispersion of the alkali-layered oxide. $Na_xMoO_3(H_2O)_y$ or $Li_xMoO_3(H_2O)_y$[7] was colloidally dispersed in water. We find that $Li_xMoO_3$ ($x$ = 0.25) spontaneously exfoliates in water to give very stable dispersions of the $MoO_3^{x-}$ layers. The layers are then are reassembled with inclusion of the pillars. This restructuring method was first demonstrated in the pillaring of $TaS_2$[8] with $Fe_6S_8(PEt_3)_6^{2+}$ and has recently been used to intercalate organic molecules in $MoS_2$.[9] The sodium compound also forms a dispersion, but our observations and recent TEM studies indicate that extensive exfoliation does not occur. This is in accordance with the lower solvation energy of the sodium cation compared to lithium. However, we find that $Na_xMoO_3$ undergoes sufficient swelling to permit direct exchange of the $Na^+$ for the polyoxycation. Solutions containing the pillaring agents were prepared by $OH^-$ hydrolysis of $AlCl_3$[10] or $Ga(NO_3)_3$ solutions.

The X-ray diffraction pattern of the oriented thin film obtained from a $Na_xMoO_3$ dispersion flocculated with $Al_{13}$ is shown in Figure 1a. The $Li_xMoO_3$-derived pattern was very similar. An average $d$ spacing of 17.94 Å was calculated from the 14 0*k*0 (00*l*) reflections. The large number of reflections, together with the small variation in their $d_{0k0}$ value (±0.03 Å) indicates that there is a high degree of order along the axis perpendicular to the layers. The interlayer expansion of 10.8 Å on pillaring is consistent with that observed for intercalation of $Al_{13}$ in smectite clays (9.6 Å)[1] and also corresponds to the van der Waals diameter of $Al_{13}$ (~10.5 Å). The degree of expansion is, to a certain extent, dependent on the topology of the layered surface and on the siting of the $Al_{13}$ cations in the interlamellar gap. Chemical (Al, Mo, Na) and thermal gravimetric analysis of the as-prepared material gave the composition $[(Al_{13})_{0.047}(Na)_{0.003}(H_2O)_{1.0}]MoO_3$, showing that virtually complete ion exchange of the interlayer alkali cations has occurred. The films were extremely stable, showing no change in the XRD pattern after several days at ambient conditions. Drying the films in air at 100 °C for 2 days resulted in a decrease in the $d$ spacing to 17.35 Å (14 sharp 0*k*0 reflections, as before). Calcination at higher temperatures shows that a layered structure ($d$ = 15.2 Å) is still present up to 350–400 °C but that interlayer collapse begins to occur at higher temperatures. The surface area [BET ($N_2$)] of the calcined material (200–250 °C) was 107 $m^2/g$. The surface area of the unpillared material (5 $m^2/g$) was negligible by comparison. Analysis of the pore size distribution showed that both micro and meso pores were present, with the surface area

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