Table I

	yield, %			
expt	12	9	6	sucrose octaacetate
A		3-5	62	5-6
B	trace	50-55	20	1-2
C	7-10	45-50	3-5	trace

rings of interest as specific metal ion complexants or chiral, synthetic intermediates.

Diacetal **5** has the eight-membered ring in a boat–chair conformation (**5a**) and possesses eight chiral centers. Its ready accessibility at low cost suggests that it may have significant potential as a precursor for synthesis.

Experimental Section

Evaporations were performed under diminished pressure. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer Model 141 polarimeter in 1-dm tubes. Column chromatography was performed with Kieselgel (Merck, 70–230 mesh) and TLC with silica gel 60 F-254 (Merck), with detection by charring with sulfuric acid.

Analytical Evaluation of the Acetonation of Sucrose with 2-Methoxypropene. Solutions of sucrose (2.5 g) in dry *N,N*-dimethylformamide (150 mL) containing ~10 mg of *p*-toluenesulfonic acid and Drierite (1 g) were stirred at 0–5 °C with the addition of 2 molar equiv of 2-methoxypropene. After 2 h of reaction, one experiment (A) was terminated, and to two remaining experiments (B and C) was added a further 2 molar equiv of 2-methoxypropene, and stirring was continued for a further 2 h, whereupon the second experiment (B) was terminated. An additional 2 molar equiv of 2-methoxypropene was added to the remaining experiment (C), and the reaction was terminated after a further 2 h of stirring of 0–5 °C.

Aliquots of the terminated reaction mixtures were per(trimethysilylated) with Tri-Sil Z (Pierce Chemical Co.), the products were analyzed by GLC in a column of OV-1 (2%) operated at 220 °C, and the observed peaks were compared with those given by reference samples of octakis(trimethysilyl)sucrose, the hexakis(trimethylsilyl) ether (**8**) of 4,6-*O*-isopropylidenesucrose (**4**), and the tetrakis(trimethylsilyl) ether (**10**) of 2,1′:4,6-di-*O*-isopropylidenesucrose (**5**), whose retention times were in the order **10** > **8** > octakis(trimethylsilyl)sucrose. Experiment A showed three peaks, the major one (~70%) corresponding to **8** and the minor ones (~15% each) to **10** and octakis(trimethylsilyl)sucrose. The peak for **10** was preponderant (~70%) in experiment B, about 20% of **8** was present, and the sucrose ether was very minor. A minor, fast-migrating peak was also observed. The diacetal derivative **10** was the principal product (~80%) in experiment C. Peaks for **8** and octakis(trimethylsilyl)sucrose were negligible, but the fast-moving peak, eluted before **10**, had increased to ~15%; this component was considered to be 2,1′:4,6-di-*O*-isopropylidene-6′-*O*-(1-methyl-1-methoxyethyl)-2,2′,3′-tri-*O*-(trimethylsilyl)sucrose (**11**) from further evidence described next.

Each of the reactions (A–C) was terminated by addition of anhydrous sodium carbonate (~3 g) and stirring for 1 h at 0 °C. The mixtures were filtered, the filtrates evaporated, and the residues acetylated with acetic anhydride–pyridine. The acetylated product mixtures were resolved by column chromatography on silica gel with ethyl acetate–petroleum ether (bp 40–65 °C) mixtures as the eluant. (Some decomposition of the products was observed when contact with the silica gel was prolonged, and this could be retarded by inclusion of a few drops of trimethylamine in the eluant.)

Four separate compounds were isolated pure from the chromatographic separations. In the order of increasing elution times, these were 3,2′,3′-tri-*O*-acetyl-2,1′:4,6-di-*O*-isopropylidene-6′-*O*-(1-methyl-1-methoxyethyl)sucrose (**12**), the diacetal tetraacetate **9**, the monoacetal hexaacetate **6**, and sucrose octaacetate. The last three compounds were each identified by direct comparison with the known reference compounds and gave ^{1}H NMR spectra free from extraneous peaks and identical with those of authentic samples. The isolated yields of the four products in the three experiments were as shown in Table I.

The ^{1}H NMR spectrum of **12** (in $CDCl_3$, C_6D_6, and Me_2CO-d_6) showed the following principal signals: δ 1.2–1.5 (18 H, $3CMe_2$), 2.0–2.2 (9 H, 3 peaks, 3OAc), 3.2 (3 H, OMe), 3.4–4.4 (m, 10 H), 5.2 (d, 1 H, $J_{3',4'}$ = 6.5 Hz, H-3′), 5.3 (apparent t, 1 H, $J_{2,3} \approx J_{3,4} \approx 9$ Hz, H-3), 5.6 (dd, 1 H, $J_{3',4'}$ and $J_{4',5'}$, 6.5 and 4.8 Hz, H-4′), 6.2 (d, 1 H, $J_{1,2}$ = 3.5 Hz, H-1).

Compound **12** was a syrup that was not very stable; after some weeks of storage at 0 °C, its NMR spectrum showed evidence of substantial decomposition.

Preparative Conversion of Sucrose (1) into 3,3′,4′,6′-Tetra-*O*-acetyl-2,1′:4,6-di-*O*-isopropylidenesucrose (9). A solution of sucrose (34.2 g, 0.1 mol) in dry *N,N*-dimethylformamide (400 mL) containing molecular sieve pellets ($^1/_{16}$ in., Type 3 A) was stirred with 2-methoxypropene (60.5 mL, 0.5 mol) in the presence of *p*-toluenesulfonic acid (25 mg) for 40 min at 70 °C. The mixture was cooled to room temperature and then treated with acetic anhydride (150 mL) and pyridine (400 mL) for 24 h at room temperature. TLC (6:1 ether–petroleum ether) showed a fast-moving, major product. The solution was evaporated, with addition of toluene during evaporation, to give a syrup that crystallized from ether–petroleum ether to give **9**: yield 46.5 g (70%); mp and mmp 136–137 °C; $[\alpha]_D$ +13° (*c* 1, chloroform). The physical constants and ^{1}H NMR spectrum of **9** were identical with those of an authentic sample.[13,17]

Preparative Conversion of Sucrose (1) into 4,6-*O*-Isopropylidenesucrose (4). A solution of sucrose (34.2 g, 0.1 mol) in dry *N,N*-dimethylformamide (400 mL) containing molecular sieve pellets ($^1/_{16}$ in., Type 3 A) was stirred with 2-methoxypropene (12.1 mL, 0.13 mol) in the presence of dry *p*-toluenesulfonic acid (25 mg) for 40 min at 70 °C, cooled to room temperature, and made neutral with anhydrous sodium carbonate. The inorganic residue was filtered off and the filtrate evaporated to a syrup. Elution of the syrup from a column of silica gel with 1:1 ethyl acetate–acetone afforded the diacetal **5** as a syrup: 3 g (7%); $[\alpha]_D$ +25.5° (*c* 1, methanol). Further elution gave the major product **4**: yield 23 g (60%); white powder; $[\alpha]_D$ +45.4° (*c* 1, methanol).

Treatment of **4** (1 g) with acetic anhydride (4 mL) in pyridine (10 mL) gave 2,3,1′,3′,4′,6′-hexa-*O*-acetyl-4,6-*O*-isopropylidenesucrose (**6**): 1.82 g (94%); $[\alpha]_D$ +45.4° (*c* 1, chloroform) [lit.[15] $[\alpha]_D$ +46.0° (*c* 0.2 chloroform). The ^{1}H NMR and mass spectra of **6** were identical with those of an authentic sample.[15]

Conventional benzoylation of **4** with benzoyl chloride in pyridine gave the crystalline 2,3,1′,3′,4′,6′-hexa-*O*-benzoyl-4,6-*O*-isopropylidenesucrose (**7**): mp 170–172 °C (from ethanol); $[\alpha]_D$ +47.2° (*c* 1, chloroform) [lit.[15] mp 168–170 °C; $[\alpha]_D$ +46.0° (*c* 1, chloroform)]. The ^{1}H NMR and mass spectra were identical with those of an authentic sample.[15]

Acetylation of the solid diacetal **5** with acetic anhydride–pyridine gave the known,[13,17] crystalline 3,3′,4′,6′-tetra-*O*-acetyl-2,1′:4,6-di-*O*-isopropylidenesucrose (**9**), mp and mmp 136–137 °C (from ether–petroleum ether).

Registry No. **1**, 57-50-1; **4**, 71196-27-5; **5**, 67909-39-1; **6**, 60825-18-5; **7**, 60825-19-6; **8**, 78479-74-0; **9**, 57471-93-9; **10**, 78479-75-1; **11**, 78498-50-7; **12**, 78479-76-2; 2-methoxypropene, 116-11-0; octakis(trimethylsilyl)sucrose, 19159-25-2; sucrose octaacetate, 126-14-7.

Peri-Bridged Naphthalenes. 5. Improved Synthesis of 1-Thiaphenalene

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We had been interested in the synthesis of aromatic chalcogen-containing organic compounds such as **1** and its selenium and tellurium analogues because of their possible incorporation into "one-dimensional" solids.[1] This interest

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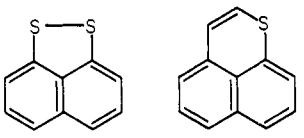


1 2

led us to reinvestigate the synthesis of 1-thiaphenalene (2), isoelectronic with structure 1. Although independent syntheses of 1-thiaphenalene had been reported by Tilak[2,3] and by O'Brien,[4] neither of these provides an efficient route to this material. We now report a convenient synthesis of 2, as well as the preparation of the hexafluorophosphate salt of its radical cation.

The starting material, 2-chloro-1-thionaphthol (3), was prepared as previously described[3] and purified by sublimation. Condensation of 3 with chloroacetic acid in alkaline solution gave 2-chloro-1-naphthyl-thioacetic acid (4)[5] in quantitative yield (See Scheme I). The transformation of 4 to the tricyclic ketone 6 was made in an overall yield of 69% by converting acid 4 to the corresponding acid chloride 5 with phosphorus pentachloride in refluxing benzene, followed by Friedel–Crafts cyclization with aluminum chloride in benzene. When 6 was treated with *p*-toluenesulfonyl hydrazide in refluxing alcohol, the corresponding *p*-tosylhydrazone, 7, precipitated quantitatively. Olefin formation was efficiently carried out by treatment of tosylhydrazone 7 with 2 equiv of *n*-butyllithium in the presence of TMEDA. 9-Chloro-1-thiaphenalene (8) was obtained in 58% yield after sublimation. Finally, the reaction of 8 with cuprous oxide in refluxing acetic anhydride–pyridine gave 1-thiaphenalene (2) in 73% yield.[3]

The cyclic voltammogram of 1-thiaphenalene in butyronitrile containing 0.1 M tetrabutylammonium tetrafluoroborate shows anodic current peaks at $E_{pa}^{1} = 0.581$ V and $E_{pa}^{2} = 0.695$ V vs. an $Ag/AgNO_3$ standard electrode. This cyclic voltammogram indicates two reversible one-electron oxidations of 1-thiaphenalene.

Attempted donor–acceptor complex formation between 1-thiaphenalene and TCNQ was unsuccessful due to the instability of the resulting complex. However, a black 1:1 1-thiaphenalene–PF_6 complex was prepared electrochemically in 0.1 M tetrabutylammonium hexafluorophosphate in methylene chloride. The room-temperature resistivity, ρ_{RT}, of this salt (micropellet) is 6×10^7 Ω cm.

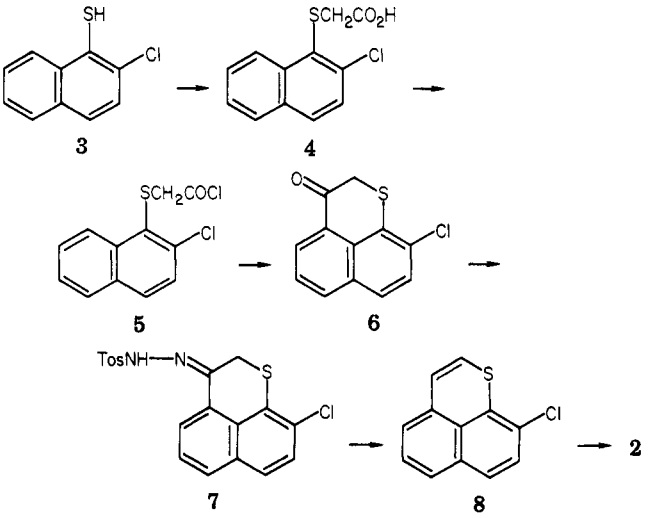
Experimental Section

2-Chloro-1-thionaphthol (3). This compound was prepared as described by Tilak.[3]

(2-Chloro-1-naphthyl)thioacetic Acid (4). To 20 mL of 10% aqueous sodium hydroxide solution was added 390 mg (2 mmol) of 2-chloro-1-thionaphthol. The mixture was stirred for 15 min, treated with 208 mg (2.2 mmol) of chloroacetic acid and refluxed for 4 h. After acidification with 2 N HCl, the solution was extracted with ether, and the ether solution was dried and concentrated. The resulting residue was recrystallized from benzene–cyclohexane to give white crystals of 4 (501 mg) in quantitative yield; mp 93–95 °C (lit.[5] mp 95–97 °C).

9-Chloro-2,3-dihydro-1-thiaphenalen-3-one (6). Into 10 mL of benzene were introduced 622 mg (2.5 mmol) of (2-chloro-1-naphthyl)thioacetic acid and 600 mg of phosphorus pentachloride. The mixture was refluxed for 30 min. The benzene and phosphorus oxychloride were then evaporated in vacuo, leaving a crude crystalline acid chloride. This was dissolved in 20 mL of benzene and treated with 400 mg of aluminum chloride over a period of 30 min. After being stirred for an additional 4 h, the reaction mixture was decomposed with ice and concentrated HCl. It was then extracted with 40 mL of benzene, and the benzene solution was washed repeatedly with 40 mL of water, decolorized, and dried. It was then concentrated to a volume of 25 mL. Hexane (80 mL) was added, and the solution was cooled to cause precipitation of the desired product. Further recrystalization from hexane gave 405 mg (69%) of 6; yellow crystals; mp 147 °C; ^{1}H NMR ($CDCl_3$) δ 3.80 (s, 2 H), 7.23–7.74 (m, 3 H), 8.00–8.29 (four groups of doublets, 2 H); IR (KBr) 1678 (carbonyl group) cm^{-1}; mass spectrum, *m/e* (relative intensity) 238 (5), 237 (6), 236 (46), 235 (18), 234 (100), 209 (31), 207 (88). Anal. Calcd for $C_{12}H_7ClOS$: C, 61.41; H, 2.98; Cl, 15.14; S, 13.65. Found: C, 61.35; H, 3.04; Cl, 15.30; S, 13.51.

Scheme I



9-Chloro-2,3-dihydro-1-thiaphenalene-3-tosylhydrazone (7). A mixture of 1.05 g (4.5 mmol) of 6, 1.1 g (5.4 mmol) of *p*-toluenesulfonyl hydrazide, and 100 mL of absolute alcohol was refluxed for 6 h, brought back to room temperature, and then filtered. The residue was washed with 95% ethanol and dissolved in the minimum amount of Me_2SO (ca. 5 mL). The Me_2SO solution was decolorized and filtered. Reprecipitation occurred when the resulting Me_2SO solution was treated with 80 mL of 95% ethanol to yield 1.80 g (100%) of 7 as a white solid: mp 229 °C dec; ^{1}H NMR (Me_2SO-d_6) δ 2.38 (s, 3 H), 3.99 (s, 2 H), 7.40–7.91 (m, 8 H), 8.06 (dd, 1 H, J = 7.5, 1.5 Hz), 10.96–11.29 (br, 1 H, NH); mass spectrum, *m/e* (relative intensity) 278 (6), 246 (6), 220 (38), 219 (18), 218 (100), 183 (20), 182 (15), 156 (13), 139 (31). Anal. Calcd for $C_{19}H_{15}ClN_2O_2S_2$: C, 56.65; H, 3.73; Cl, 8.82; N, 6.96; S, 15.90. Found: C, 56.49; H, 3.82; Cl, 8.66; N, 6.78; S, 15.87.

9-Chloro-1-thiaphenalene (8). To a solution of 804 mg (2 mmol) of 7 in 50 mL of dry benzene and 1.5 mL of TMEDA under argon atomsphere was added 2.2 mL (4.4 mmol) of *n*-BuLi (2.0 M in hexane) with continuous stirring. The mixture was stirred at room temperature until the suspension disappeared, which required a period of 24 h. After being quenched with water, the reaction mixture was extracted with ether and dried over $MgSO_4$. The resulting ether solution was concentrated and filtered through an alumina column with benzene–hexane (1:1) as the eluant to give a yellow solid, which was sublimed at 70 °C (0.03 mmHg) to yield 253 mg (58%) of 8 as light yellow crystals: mp 112 °C (lit.[3] mp 121 °C); ^{1}H NMR ($CDCl_3$) δ 6.29 (d, 1 H, J = 10.8 Hz), 6.58 (d, 1 H, J = 10.8 Hz), 6.82 (dd, 1 H, J = 8.2 Hz, 2 Hz), 7.10–7.46 (m, 4 H).

1-Thiaphenalene (2). The procedure used for the dechlorination of 8 was a slight modification of Tilak's method.[3] A mixture of 654 mg (3 mmol) of 8, 10 mL of acetic anhydride, 1.6 g of cuprous oxide, and 3 mL of pyridine was refluxed for 22 h. The mixture was cooled to room temperature, poured slowly into ammonium hydroxide solution, and filtered, and the precipitate

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was washed with benzene. The resulting solution was extracted with chloroform, and the chloroform extract was washed with water, dried, and concentrated. The crude product was chromatographed on silica gel with 1:10 chloroform–hexane as the eluant to afford 403 mg (73%) of 1-thiaphenalene. Further purification by sublimation at 60 °C (0.03 mmHg) yielded light yellow crystals of **2**: mp 120 °C (lit. mp 124 °C,[3] 120–122 °C[4]); ^{1}H NMR ($CDCl_3$) δ 6.10 (d, 1 H, J = 9.6 Hz), 6.41 (d, 1 H, J = 9.6 Hz), 6.69 (dd, 1 H, J = 7.1, 2 Hz), 6.82–7.34 (m, 5 H); mass spectrum, m/e (relative intensity) 186 (5), 185 (13), 184 (100), 183 (12), 152 (37), 151 (8), 139 (31); IR (CCl_4) 3050, 1635, 1570, 1435, 1377, 1368, 1330, 960 cm^{-1}. Anal. Calcd for $C_{12}H_8S$: C, 78.26; H, 4.35; S, 17.39. Found: C, 78.39; H, 4.31; S, 17.52.

1-Thiaphenalene Hexafluorophosphate. Into a H-tube fitted with a medium-porosity glass frit in the bridge and containing 0.1 M tetrabutylammonium hexafluorophosphate in methylene chloride was placed 5 mg of **2** in one side of the tube. The tube was then attached to platinum electrodes connected to a 3-V battery (positive electrode in the side containing **2**). After a period of 7 days, the 1-thiaphenalene hexafluorophosphate was collected from the electrode. It was washed twice with a small portion of acetonitrile to give a black powder. Anal. Calcd for $C_{12}H_8F_6PS$: C, 43.77; H, 2.43. Found: C, 44.71; H, 2.64. The lack of material precluded the possibility of obtaining duplicate or more accurate analysis.

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Registry No. **2**, 203-93-0; **2** radical cation PF_6^-, 78167-10-9; **3**, 78167-11-0; **4**, 78167-12-1; **5**, 78167-13-2; **6**, 78167-14-3; **7**, 78167-15-4; **8**, 78167-16-5.

(Dimethylthiocarbamoyl)thio Group as a Protecting Group of Phosphates in Oligonucleotide Synthesis via the Phosphotriester Approach[1]

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It has been shown by several workers[2] that a nucleoside 3′-phosphotriester is a key intermediate in the synthesis of oligonucleotide by the improved phosphotriester method. Recently, it has been demonstrated in our laboratory that 5′-*O*-(dimethoxytrityl)-2′-*O*-tetrahydropyranylnucleoside 3′-(4-chlorophenyl 5-chloro-8-quinolyl) phosphates are key intermediates in the synthesis of Rous Sarcoma virus 35S RNA by the improved phosphotriester method.[3] More recently, we have found that 5′-*O*-(methoxytrityl)deoxyribonucleoside 3′-[2-cyanoethyl *S*-(dimethylthiocarbamoyl) thiophosphates] **2** are key intermediates in the synthesis of deoxyribonucleotides by the improved phosphotriester method. The (dimethylthiocarbamoyl)thio group is stable to acid and alkali solutions,[4] removal being achieved specifically by treatment with boron trifluoride in a mixture of dioxane and water (9:1 v/v).

Table I. Reaction Conditions and Yields for the Synthesis of Nucleoside 3′-Phosphotriesters **2**[a]

step 1				step 2		
mmol	pCe, mmol	QS, mmol	time, h	$(Me_2NCSS)_2$-Ph_3P, mmol	time, h	yield, %
MMTrT						
0.50	0.55	1.10	12	0.55	24	21
0.50	0.55	1.10	12	1.65	24	68
0.50	0.55	1.65	12	1.65	24	35
0.50	0.45	0.90	12	2.25	24	67
1.00	1.10	2.20	12	5.50	24	88
d-MMTr(anC)						
1.00	1.10	2.20	12	5.50	24	85
d-MMTr(bzA)						
1.00	1.10	2.20	12	5.50	24	79
d-MMTr(ibuG)						
1.00	1.10	2.20	18	5.50	24	68

[a] MMTr = monomethoxytrityl; pCe = 2-cyanoethyl phosphate; QS = 8-quinolinesulfonyl chloride.

In the present paper, we describe the synthesis of deoxyribooligonucleotides using the (dimethylthiocarbamoyl)thio group as a new protecting group on phosphates in internucleotidic bonds.

We first examined preparation of 5′-*O*-(methoxytrityl)deoxyribonucleoside 3′-[2-cyanoethyl *S*-(dimethylthiocarbamoyl) thiophosphates] **2**.

5′-*O*-(Methoxytrityl)thymidine (1.0 mmol) was treated with 2-cyanoethyl phosphate (1.1 mmol) in the presence of 8-quinolinesulfonyl chloride (QS)[5] (2.2 mmol) in dry pyridine. After 12 h, TLC shows that the phosphorylation was completed. To the reaction mixture were added bis(dimethylthiocarbamoyl) disulfide (5.5 mmol) and triphenylphosphine (5.5 mmol). The mixture was kept for 24 h at room temperature. After the usual workup, the fully protected mononucleotide **2a** was isolated in high yield by silica gel column chromatography (see Table I). In the above reactions, the use of a slight excess of nucleoside over 2-cyanoethyl phosphate gave a poorer yield of **2a**. Furthermore, when the isolated phosphodiester **1a** was allowed to react with bis(dimethylthiocarbamoyl) disulfide and triphenylphosphine, the yield of **2a** decreased to 45% yield. From above facts, when we speculate on the mechanism for the phosphorylation, the following scheme may be most plausible at present (Scheme I).

We next examined the synthesis of dinucleotide **5** and trinucleotide **7** by using **2**. The phosphotriester **2a** was treated with 2% benzenesulfonic acid in a mixture of di-

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