Bulk pyrolysis of $(Ph_3P)_2CuIn(SeEt)_4$ in a Pyrex tube at 400–450 °C and 0.01 mmHg of pressure gives shiny films of single-phase $CuInSe_2$ as determined by the X-ray powder diffraction (XRD) pattern and confirmed by elemental analysis. Elemental analysis of the bulk $CuInSe_2$ shows less than 0.6% of carbon content. Proton NMR and mass spectra of the volatile products collected in a liquid nitrogen trap during the pyrolysis experiment show only Ph_3P and EtSeEt. Scanning electron micrographs (SEM) of $CuInSe_2$ show a smooth continuous film morphology.

The $(Ph_3P)_2CuIn(QR)_4$ compounds are the first structurally characterized examples of single-source precursors to the ternary semiconductors $CuInQ_2$. Their solubility in common organic solvents make them good candidates for solution spray pyrolysis for thin film deposition at relatively low temperatures.[18]

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Supplementary Material Available: An ORTEP drawing of compounds **2** and **3** and tables of atomic coordinates of all atoms and anisotropic and isotropic thermal parameters of all non-hydrogen atoms for **1–3** (36 pages); listing of calculated and observed $(10F_o/10F_c)$ structure factors for **1–3** (54 pages). Ordering information is given on any current masthead page.

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Selectively ^{13}C-Enriched DNA: ^{13}C and ^{1}H Assignments of the Lac Operator by Two-Dimensional Relayed HMQC Experiments

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NMR spectroscopy can provide useful conformational information on drug–DNA or protein–DNA complexes in solution.[1,2] Unfortunately the overlap of proton resonances between the two

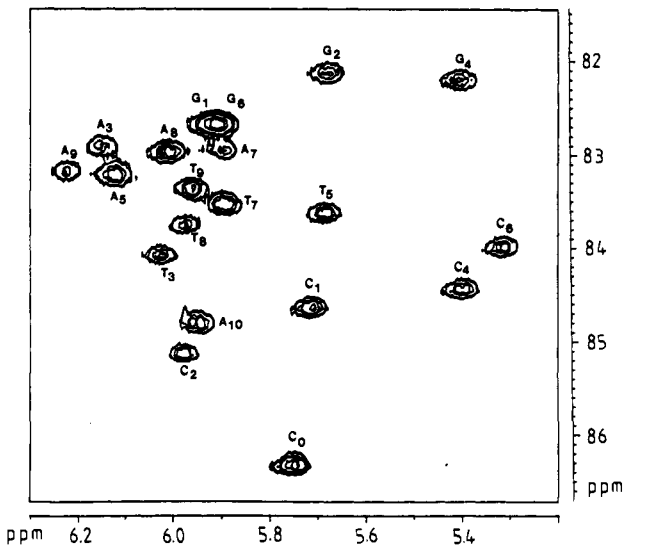

Figure 1.

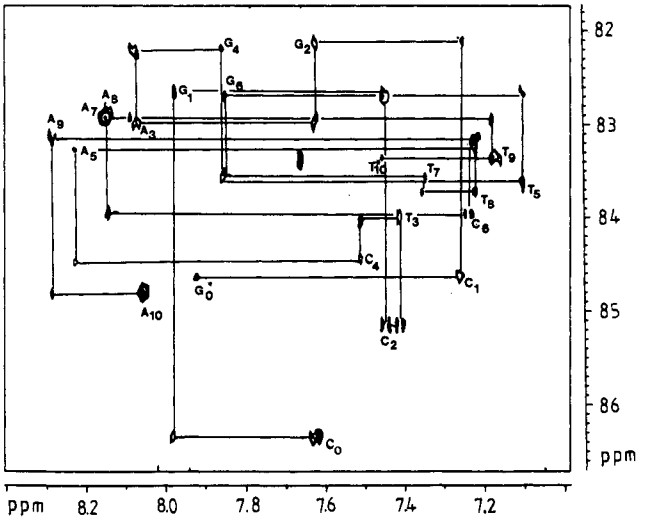

Figure 2.

partners often precludes a complete assignment. One way of circumventing this difficulty is to use complexation of nucleic acids with ^{15}N uniformly labeled proteins.[3,4] Another is to use ^{13}C-labeled nucleic acids. Nikonowicz and Pardi recently reported[5,6] the first multidimensional heteronuclear NMR studies on uniformly ^{13}C-labeled RNA duplexes prepared by enzymatic procedures. Introduction of a ^{13}C-label in selected positions of an oligo(deoxy)nucleotide, potentially available by chemical synthesis, is another solution. Within this context, labeled sugar moieties at C1′ or C2′ appeared to be the best choice since the proximity of their attached proton with the base protons allows for a complete assignment of the oligonucleotide's proton resonances.

This paper describes the ^{13}C and ^{1}H resonance assignments of half of the selectively ^{13}C-labeled lac operator at the C1′ carbon. This method, requiring relayed HMQC-TOSCY and HMQC-NOESY spectra, is promising for the study of large oligonucleotides or complexes with DNA.

The required 1′-^{13}C-labeled oligodeoxynucleotide 5′d-(CGCTCACAATT*) and its complementary sequence were prepared on a Pharmacia automatic synthesizer via phosphoramidite chemistry[7] using the classical unlabeled deoxynucleoside

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(T* or G*) CPG support and the [1'-^{13}C]-5'-*O*-dimethoxytrityl 3'-*O*-(β-cyanoethyl *N*,*N*-diisopropylphosphoramidite) building blocks.[8,13]

Assignments of the ^{13}C resonances were made by a heteronuclear experiment derived from the HMQC sequence.[14-18] The HMQC spectrum of the duplex is shown in Figure 1. Clearly, the spreading of both the H1' and C1' resonances brings about an excellent dispersion of the 20 ^{1}H1'-^{13}C1' correlations. It is well-known that, in a right-handed DNA, the H1' proton sugar (*i*) is close to the H8 or H6 nucleobase protons of the 3'-neighboring nucleotide (*i* - 1) and far from all the sugar protons of its 5'-neighboring nucleotide (*i* + 1).[19] Using this property, the sequential assignments of the ^{13}C and ^{1}H resonances were made by the C1'(*i*)-H1'(*i*) and C1'(*i*)-H1'(*i*-1) correlations on the relayed HMQC-NOESY spectrum (Figure 2). As soon as the H1' and H8-H6 resonances were assigned, the examination of the through-bond *J* coupling correlations in the HMQC-TOCSY experiment gave the H2', H2'', H3', and H4' resonance assignments. Assuming that the only sugar protons close to H1' are those belonging to their own residue (as generally observed in canonical conformations of DNA), their assignment can also be directly made on the HMQC-NOESY spectrum. For the first time to our knowledge, the resonances of C1' and all nonexchangeable protons (except for H2 and H5',5'') of an oligonucleotide were obtained using 2D relayed ^{13}C-^{1}H HMQC-NOESY and HMQC-TOCSY spectra. It should be noted that this kind of experiment, having about the same sensitivity as conventional ^{1}H-^{1}H NOESY, can be run with a small amount of ^{13}C-labeled duplex. In our example, a 0.6 mM concentration was used.

The good dispersion of the ^{1}H1'-^{13}C1' correlations is favorable for studying much longer oligonucleotides where the overlap of the H1' resonances bars the complete assignment of the proton resonances. This strategy is expected to greatly facilitate the NMR conformational studies of a nucleic acid when interacting with a ligand. Moreover, significant information on the extent and time scale of the internal dynamics for sugar units can be obtained by measuring the ^{13}C relaxation parameters. This is because the ^{13}C-selective enrichment at 100% offers the advantage of sensitivity without complicating both the spectrum by ^{13}C-^{13}C coupling constants and the analysis of T_1 or NOE data by additional ^{13}C-^{13}C relaxation pathways.

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Molecular Monolayer Rods and Tubules Made of α-(L-Lysine),ω-(Amino) Bolaamphiphiles

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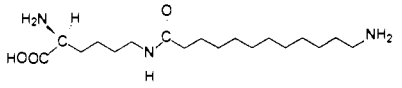
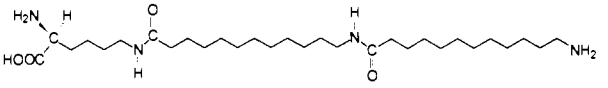
Spherical micelles and vesicles are formed from amphiphiles[1] and bolaamphiphiles[2] by the hydrophobic effect.[1] The head groups are hydrated, and their interaction is of a repulsive nature.[3] Micelles and vesicles thus have fluid character and lose their shape upon drying. Introduction of secondary amide bonds into the head groups, however, leads to strong hydrogen bond chains. The fluid micelles and vesicles are converted to solid micellar rods[4,5] and vesicular tubules.[6] Such molecular assemblies should be isolable in the dry state under favorable conditions. We have synthesized unsymmetric bolaamphiphiles **1** and **2** with one amino acid head group (D- and L-lysine or -ornithine) and one ammonium chloride head group. Electron micrographs of aqueous gels show micellar rods and, more interesting, vesicular tubules with a membrane of monomolecular thickness.



1



2

The N^{6}-acylated L-lysine **1**[7] dissolves up to 1% (10^{-2} mol L^{-1}) in water at room temperature below pH 5.5. It becomes insoluble above pH ≈ 8.5. At pH 10.5-11.0, opaque dispersions are obtained. In electron micrographs of the dried and negatively stained probes, one observes single as well as clustered micellar fibers with a diameter of 25 ± 5 Å (Figure 1). This corresponds exactly to a micellar monolayer. We assume a connecting amide hydrogen bond chain, which forms a thread along the rod axis and arranges both head groups on two different cylinders (Figure 1b). This is in loose analogy to amide bond chains found in a crystal structure of an α,ω-bis-gluconamide bolaamphiphile[8] (model A). The major binding fource should *not* originate from the hydrophobic effect, but from these hydrogen bond chains. Similar, but

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