Table II. Integrated Areas of Terminal Vinyl Protons[a]

	Peak maxima at τ		
	4.87 ppm	4.97 ppm	5.14 ppm
Calcd[b]			
(1*Z*)-Allyl-3-d_2		0.597	0.403
(1*E*)-Allyl-3-d_2	0.674		0.326
1:1 mixture	0.337	0.298	0.365
Obsd[c]			
135°	0.327 ±0.006	0.303 ±0.002	0.370 ±0.006
160°	0.326 ±0.002	0.297 ±0.002	0.377 ±0.002
180°	0.331 ±0.004	0.306 ±0.005	0.364 ±0.004

[a] Normalized to one proton. [b] Consistent results are obtained by analysis as the B part of an ABX spectrum; *cf.* J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 132. [c] Samples obtained at temperatures indicated. Each entry is the mean and standard deviation of six–eight 60-MHz scans.

Although this is now the third report of essentially stereospecific $_s2_A + _s2_S$ cleavage of a cyclobutane[24] (if also the first to include associated kinetics and activation parameters), it is apparent that failure to observe such stereospecificity is much more common.[5a,b,d–f,h] The possible origins of such diversity will need be discussed elsewhere.

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edy) its inability to disentangle cleavage specificity from that of subsequent Cope rearrangement. Isomeric intermediates were not considered. Neither was extensive mechanistic deduction thereby inhibited.

(24) The qualification of apparently incomplete stereospecificity (93–95%,[5c] *ca.* 90%[5g]) is, we suggest, more economically rationalized in footnote 15 of ref 5g than it is in the text above it.

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Synthesis and Proton Magnetic Resonance Spectrum of a Selectively Deuterated Dinucleoside Monophosphate, Adenylyl-(3′–5′)-adenosine

Sir:

Proton magnetic resonance studies have yielded much valuable information about key conformational features such as the syn–anti orientation of base and ribose rings,[1] the furanose ring conformations,[2] and the orientation of exocyclic groups[3] in a wide variety of monomeric nucleic acid constituents. It is of considerable importance to extend such detailed studies to higher oligonucleotides in order to establish the influence of chain length upon the nucleotide conformation. Although a number of initial studies along this line have been reported for selected dinucleotides,[4] the full usefulness of nmr measurements in this direction is hampered by extensive overlapping of signals that prevents complete assignments of the spectra, even at the highest operating frequencies currently available. An approach which in principle can circumvent this difficulty involves the synthesis of oligonucleotides in which one (or more) of the nucleotides is replaced by its fully deuterated analog. We have recently developed such an approach, and report the results for the dinucleoside monophosphate adenylyl-(3′–5′)-adenosine, ApA, in this communication.

An illustration of the complete 220-MHz proton spectrum for the protio form of ApA is given in Figure 1a. Assignments of the base-ring (H-2 and H-8) and ribose H-1′ signals reported in extensive earlier studies[4b,5] are essentially indirect in that they are based in part on assumed conformational models for ApA and upon results of measurements on similar model compounds. No direct assignment of the remaining ribose ring proton signals has been reported.

Figure 1b shows the spectrum for 2,1′,2′,3′,4′,5′,5′-heptadeuterioadenylyl-(3′–5′)-adenosine, *ApA, an adenine dinucleoside monophosphate in which all of the 3′ nucleotide (*Ap–) protons (except H-8) are replaced by deuterium atoms. *ApA was synthesized by condensing 2,1′,2′,3′,4′,5′,5′-heptadeuterio-*N*,$O^{2'}$,$O^{5'}$-tribenzoyladenosine 3′-phosphate[6] with *N*,*N*′,$O^{2'}$,$O^{3'}$-tetrabenzoyladenosine[7] in the presence of dicyclohexylcarbodiimide. The *ApA was purified by paper and DEAE-cellulose chromatography and the final product was identical chromatographically with a known standard ApA sample. The 2,1′,2′,3′,4′,5′,5′-heptadeuterioadenosine 3′-monophosphate used in the synthesis was isolated by the following procedures. Ribonucleic acid extracts from fully deuterated blue-green algae,[8] *Synechococcus lividus*, were hydrolyzed in alkaline solution yielding 2′,3′ mixtures of all four major ribomononucleotides. The individual 2′,3′ pairs were in turn separated by ion exchange chromatography[9] and the deuterated 3′-AMP was then separated from the 2′ isomer by paper chromatography.

A comparison of the spectra in Figures 1a and 1b permits a straightforward and direct assignment of H-2 and ribose ring proton signals to the individual

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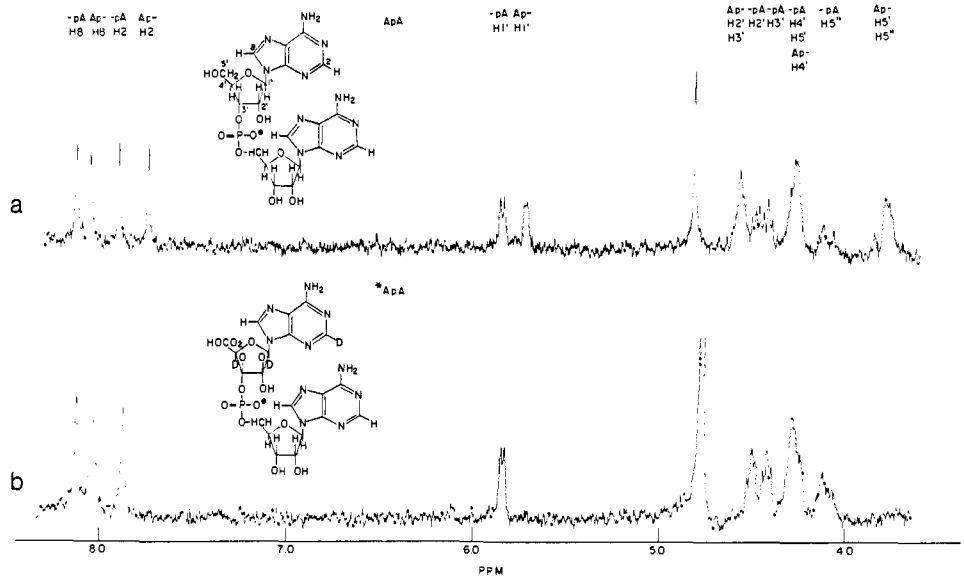

Figure 1. 220-MHz proton spectra for (a) ApA and (b) *ApA in D_2O at 18°. Solutions were prepared in 100% D_2O and samples were contained in 2 mm capillary spinning tubes. Both spectra were measured for 0.10 *M* solutions and solvent conditions (pD 6.8) and instrumental settings were the same in each case. The hydroxyl and amino proton resonances were not observed because of exchange with the solvent.

3′ and 5′ nucleotides of ApA. Direct assignment of the H-8 signals is prevented by exchange of D-8 on *Ap- with hydrogen.[10] ^1H–^1H and ^{31}P–^1H decoupling and spin tickling measurements on *ApA and ApA further establish assignments of individual signals and multiplet patterns as summarized in Figure 1 and Table I.

Table I. Assignments and Chemical Shifts[a] of the Base and Ribose Protons of ApA

Proton	Residue of ApA	
	Ap-	-pA
H-8	8.07	8.17
H-2	7.89	7.96
H-1′	5.73	5.85
H-2′	4.57	4.47
H-3′	4.57	4.39
H-4′	4.27	4.27
H-5′	3.77	4.27
H-5′′	3.79	4.08

[a] Chemical shifts are given relative to external sodium 3-trimethylsilylpropionate-*2,2,3,3-d*$_4$ (TSP) reference and are accurate to ±0.01 ppm.

The present results confirm the earlier indirect assignments of H-2 (3′ and 5′) and H-1′ (3′ and 5′), and, in this regard provide support for the stacked conformation of ApA. The data also reveal an unusually large chemical-shift nonequivalence for H-5′ and H-5′′ of -pA. A shift nonequivalence of this type is not observed for the simple mononucleotide 5′-AMP[11] and its presence in ApA suggests the possibility of conformational differences between the monomer and dimer in this region of the molecule. Finally, the present work establishes the feasibility of synthesizing oligonucleotides with fully deuterated nucleotides at known positions. Full details outlining the syntheses and conformational deductions for ApA and other dinucleotides will be published elsewhere.

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Studies in Linear Dichroism. VI.[1] On the Polarization of Electronic Transitions in Isolated Double Bonds

Sir:

There are considerable differences in the interpretation of the broad and diffuse ultraviolet spectra of isolated olefins.[2] Therefore, the origin of the Cotton effects of chiral olefins has not yet been clarified.[2d,3]

In order to get a better insight into the spectroscopic properties of isolated double bonds, we have measured their polarized (linear dichroic) spectra, *i.e.*, we have oriented olefins in stretched films and measured their uv spectra using polarized light in the direction of stretching and orthogonal to it.[1,4]

The polarized spectrum of a symmetrically substi-

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