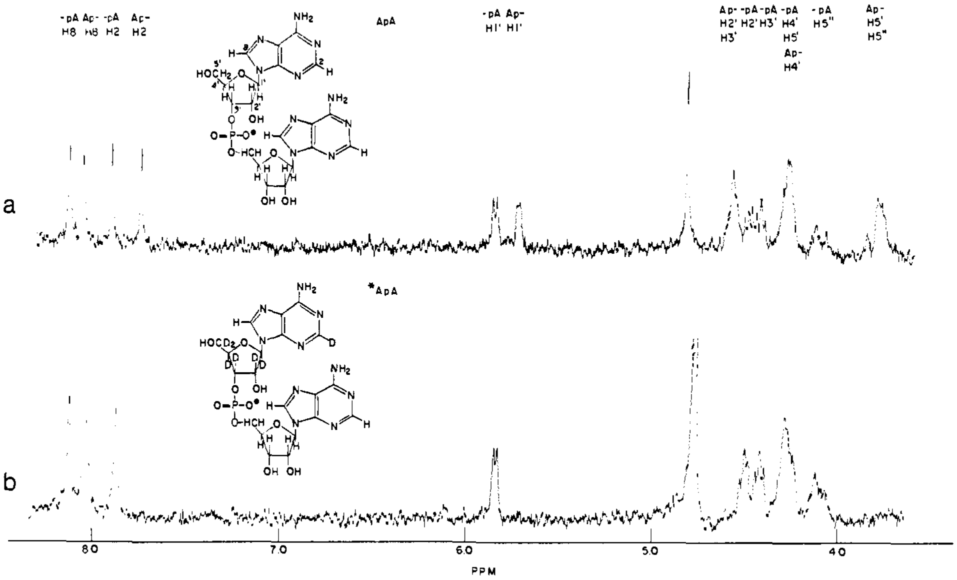

Figure 1. 220-MHz proton spectra for (a) ApA and (b) *ApA in D_2O at 18°. Solutions were prepared in 100% D_2O and samples were contained in 2 mm capillary spinning tubes. Both spectra were measured for 0.10 *M* solutions and solvent conditions (pD 6.8) and instrumental settings were the same in each 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-d₄* (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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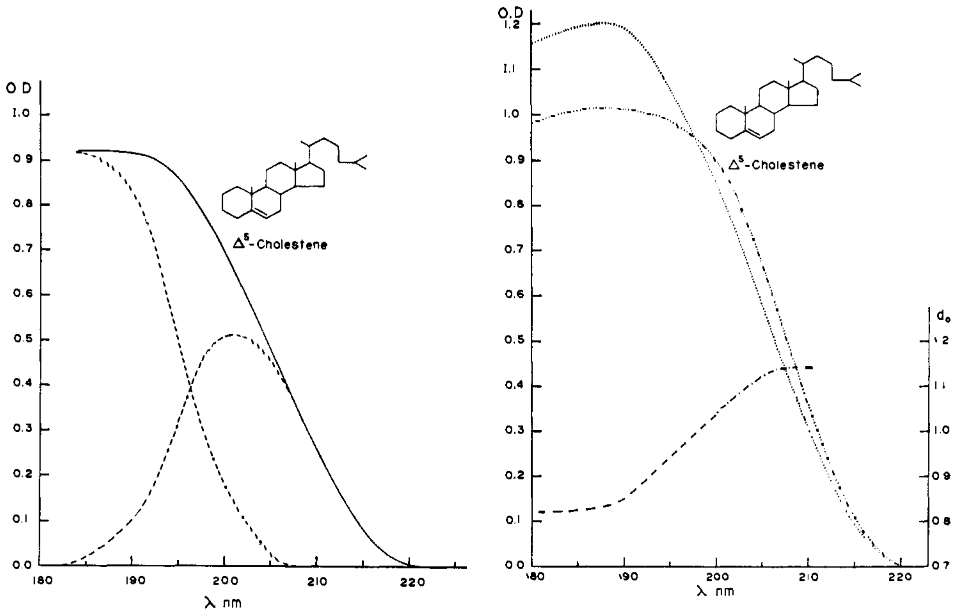

Figure 1. Δ^5-Cholestene: left, the ultraviolet spectrum (——), in unstretched polyethylene film; (----), the resolved spectrum; right, the linear dichroic spectrum (–····–), the curve of optical densities obtained by light polarized in the direction of stretching; (···), the curve obtained by light perpendicular to the direction of stretching; (–·–), the plot of the dichroic ratios ($d_0 = \epsilon_{||}/\epsilon_{\perp}$) *vs.* λ.

Table I

Compound	λ_1 band (max <190 nm) d_0[a]	α,[b] deg	γ,[c] deg	λ_2 band (max 202–205 nm) d_0[a]	α,[b] deg	γ,[c] deg
Δ^4-Cholestene	1.68	40	0	2.5	28	17
Δ^5-Cholestene	0.82	60		1.14	51	
17-Acetoxy Δ^4-Androstene	1.27	44	0	1.63	34	15
17-Acetoxy Δ^5-Androstene	0.85	61		1.14	50	

[a] Measured dichroic ratio; $\epsilon_{||}/\epsilon_{\perp}$. [b] The angle between the direction of the transition moment and the molecular axis. [c] The angle between the direction of the transition moment and the double band.

tuted olefin, bicyclohexylidene, which has two bands of similar intensity at λ_{max} 208 and ~185 nm (ϵ 8000 and 7700) was found to be wavelength independent. Both bands show similar dichroic ratios, the ratios of the extinction coefficients for the two orthogonal incident light polarizations, and are thus equally polarized. Since the direction of the longitudinal axis in this compound is along the double bond, both transitions will be polarized along this bond.[5] However, the unsymmetrically substituted olefins, Δ^4- and Δ^5-cholestenes, showing only one broad absorption band in the uv with λ_{max} ~190 nm (ϵ 8000–10,000)[7] (Figure 1), exhibit wavelength-dependent linear dichroic spectra. A plot of dichroic ratios d_0 *vs.* λ (Figure 1) gives for both compounds S-shaped curves, indicating two overlapping bands, λ_1 and λ_2, at shorter and longer wavelengths, respectively. In the regions where the d_0 values are wavelength independent, the bands are considered to be pure. Using these values of the dichroic ratios we were able to separate the isotropic uv spectra of Δ^4- and Δ^5-cholestenes and of additional steroidal olefins. These results indicate that the broad uv spectrum of the isolated double bond is in fact a superposition of two closely lying transitions λ_1 and λ_2 having also extinction coefficients of the same order of magnitude.

In order to establish the direction of the transitions in the Δ^4- and Δ^5-cholestenes, we applied the previously described model of orientations of molecules in the stretched films.[4] Using this model and the d_0 values (Table I), we have attempted to calculate the angles between the transition moment and molecular axis.

It is further apparent from X-ray data[8] that the double bond in Δ^5-cholestene is not twisted and is located in the "best plane" of the molecule and forms an angle of *ca.* 60° with its molecular axis.

In Δ^4-cholestene the plane of the double bond makes a dihedral angle of 40° with the "best plane" of the molecule, and the projection of the double bond axis on this plane forms an angle of 0° with the molecular axis.

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(4) For the method, instrumentation, and uses *cf.* A. Yogev, L. Margulies, D. Amar, and Y. Mazur, *J. Amer. Chem. Soc.*, 91, 4558 (1969); A. Yogev, J. Riboid, J. Marero, and Y. Mazur, *ibid.*, 91, 4559 (1969); A. Yogev, L. Margulies, and Y. Mazur, *ibid.*, 92, 6059 (1970); A. Yogev, L. Margulies, and Y. Mazur, *Chem. Phys. Lett.*, 8, 157 (1971).

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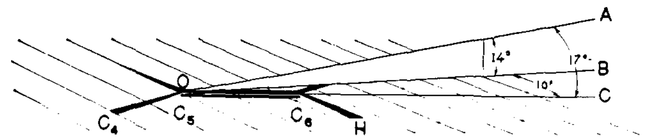

Figure 2. Schematic view of the transition moments of the two bands in Δ^5-cholestene: O–C, the direction of polarization of λ_1 (the shorter wavelength) band; O–A, the direction of polarization of λ_2 (the longer wavelength) band; O–B, the projection of the direction of polarization of the λ_2 band on the plane of the double bond; AOC, the angle between the transition moment of the λ_2 band and the double bond axis; BOC and AOB, the respective in-plane and out-of-plane deviations from the double bond axis of the transition moment of the λ_2 band.

These figures are based on the X-ray data for Δ^4-3-keto steroids.[9,10]

Calculations of the directions of the λ_1 and λ_2 transitions were performed geometrically using the values of angles these transitions make with the molecular axis (angles α, Table I), the previously mentioned X-ray data, and the assumption that these λ_2 and λ_1 transitions form similar angles with the double bond axis in both Δ^5- and Δ^4-cholestenes.

Since the α angles for λ_1 transitions in Δ^5- and Δ^4-cholestenes are 60 and 40°, respectively (Table I), it follows that the polarization of this transition is along the double bond axis. On the other hand, it is clear from the data of Table I that the λ_2 transition cannot be along the double bond axis.

Using similar geometrical consideration we have found that the λ_2 transition forms an angle of *ca.* 17° with the double bond axis, and an angle of 14° with the plane of the double bond; the projection of this transition on the double bond plane falls at an angle of 10° with the axis of the double bond (Figure 2).

The same directions for the transition moments were obtained also for Δ^4- and Δ^5-androstene derivatives which posses different orientations in the stretched films than those of the corresponding cholestenes (Table I).[11]

Thus, we may conclude that olefins having symmetrically substituted double bonds show in the uv two bands of similar intensity, both of which are polarized along their double bond. In the unsymmetrically substituted olefins, however, only the shorter wavelength band, λ_1, has in all cases a transition moment direction along the double bond, whereas in the longer wavelength band, λ_2, the transition moment may deviate from this direction.

It is highly probable that the shorter wavelength band, λ_1, is the conventional valence shell π_z–π_z* transition, whose polarization remains along the double bond and is not affected by unsymmetrical substitution.

However, the assignment of a transition to the λ_2 band is more problematic. We can rule out, for this band, the Rydberg type π–3s (π_z–σ*),[2f] the valence shell σ–π*,[2e] or any other transition whose polarization should be perpendicular to the plane of the double bond.[2g]

It was proposed by Clark[6] that the higher wavelength band in a symmetrically substituted olefin, bicyclohexylidene, corresponds to a σ–σ* transition which is polarized along the double bond. Very recently Buenker, Peyerimhoff, and Hsu[12] suggested that a high intensity and low energy band in ethylene, which may be correlated with our λ_2 band, is due to the Rydberg type π–3p_y transition (π_z–π_y*) of ^1B_g symmetry. This transition is formally allowed only in olefins twisted in the ground state and thus corresponds to a nonvertical transition in planar olefins. It may be expected that the unequal substitution of the double bond will have greater effect on the polarization of this Rydberg type band than on the valence type π_z–π_z* band.

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[11] Since X-ray data are not available for other steroidal olefins, we have estimated polarization of some of them using Dreiding models. We have also found that in these compounds the λ_1 transitions are polarized along the double bond, but that the polarization of the λ_2 transition may assume other directions as well.

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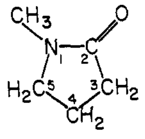
Barrier to Internal Rotation in *N*-Methylpyrrolidone[1]

Sir:

We wish to report the first known case of a methyl rotor attached to an intrinsically asymmetric framework with a nearly zero barrier to internal rotation.[2] The far-infrared spectrum of *N*-methylpyrrolidone (I) shows a vast series of bands, at least one every wave number below 350 cm^{-1}. Such a large number of bands for a molecule of this size could only come from one of two possible kinds of motion, nearly free pseudorotation[3] of the ring as a whole or nearly free internal rotation of the methyl group. However, the nitrogen–carbon amide bond is thought to be partially double bond in character and is expected to have a very high torsional force constant. This would rule out a free pseudorotation. Nearly free internal rotation is the only remaining possibility.



(I)

The spectrum of I in benzene shows intense peaks at about 175 and 310 cm^{-1} and a series of weaker bands extending down to the lower wavelength limit of our spectrometer. The 175-cm^{-1} band is assigned as ring bending (the out-of-plane motion of methylene group 4) and the 310-cm^{-1} band as the twisting motion of the ring (methylene group 3 moves above the plane while methylene group 5 moves below it and the amide group twists in the opposite sense). The solution

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[1] Supported in part by the National Science Foundation.

[2] Methyl isocyanate with a barrier of 49 cal/mol [R. F. Curl, Jr., V. M. Rao, K. V. L. N. Sastry, and J. A. Hodgeson, *J. Chem. Phys.*, 39, 3335 (1963)] can be thought of as a slightly perturbed linear molecule; *m*-fluorotoluene with a barrier of about 47 cal/mol [H. O. Rudolph, and A. Trinkaus, *Z. Naturforsch.*, *A*, 23, 68 (1968)] as a perturbed toluene.

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