it is possible to observe the reaction of the brosylate to form a species, VI, whose spectrum is very similar to that shown in Figure 1: τ 2.1–2.5 (quartet, four protons), 4.29 (triplet, two protons), 6.10 (triplet, two protons), 6.94 (singlet, three protons), and 7.48 (pentuplet, two protons). We conclude that an oxonium ion is formed in this system as well, and make the spectral assignments by analogy to those made for IIb. It is important to notice the presence of a phenyl substituent is not necessary for ion formation.

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A Hypochromic Effect from Pairing of Purine and Pyrimidine Bases

Sir:

Hypochromism in nucleic acids was first theoretically considered by Tinoco[1,2] and Rhodes[3] and was attributed to a dispersion interaction involving the transition moment for the lowest energy $\pi-\pi^*$ transition with those for the transitions of higher energy. It has consequently been generally supposed that hypochromism is a consequence of "vertical," or stacking, interactions between the chromophores, and indeed the spectra of polynucleotides in the single-strand stacked conformation[4,5] bears out the validity of this concept. At the same time it is known that intensity changes can come about from environmental effects of various kinds; we have attempted to ascertain whether such extraneous factors can lead to hypochromism contributions in consequence merely of base pairing.

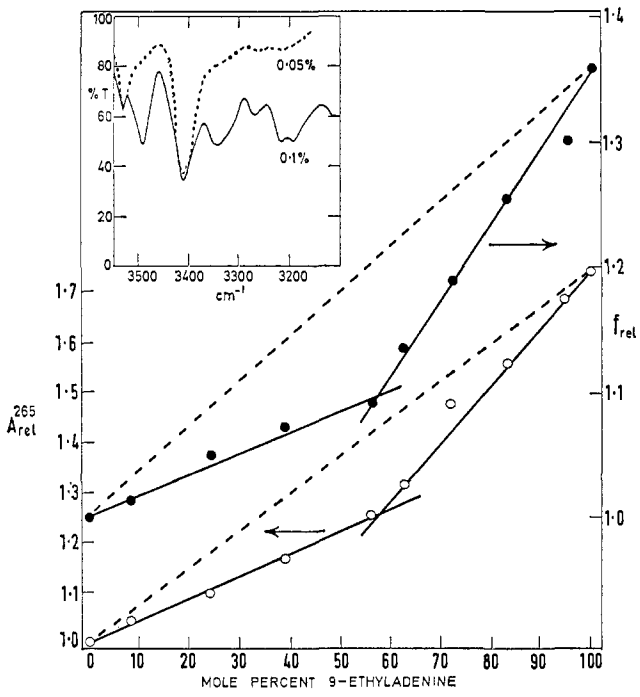

Figure 1. Absorbances and oscillator strengths, relative to 1-cyclohexyluracil, of 9-ethyladenine and 1-cyclohexyluracil mixtures. Solutions of the two bases *ca.* 0.03 *M*; solvent, chloroform; path, 0.033 mm. Inset: infrared spectra of a 1:1 mixture at similar concentration (1-mm path) showing association, and at low concentration (1-cm path) showing negligible association. Qualitatively similar results were obtained with 1-*n*-octadecyluracil and 9-*n*-octadecyladenine.

Figure 1 shows relative absorbances of A + U mixtures in chloroform solution at the highest workable concentration, as well as relative oscillator strengths (taken to 4.3×10^4 cm^{-1}). It is consistently found that a hypochromic effect is present, falling in magnitude with diminishing concentration, but still measurable at 0.02 *M* in A. The point of maximum hypochromicity is displaced from A:U equivalence in the sense predicted by the presence of A_2 dimers, but this effect is close to the limits of error. From the infrared study, we find that in a 1:1 mixture of A + U, *ca.* 0.03 *M* in each, some 40% of the A is present as A···U pairs, and about one-third of the remainder as A_2. Thus for complete pairing a hypochromic decrease in oscillator strength of around 20% is predicted. It must be stated that these results are regarded as only semiquantitative since the solutions in the spectrophotometers were not thermostated. In the Beckman instrument, the temperature in the sample compartment is about 32°.

We next consider the effect of hydrogen bonding on the A and U spectra *per se*. It is remarkable that the U spectrum shows no significant perturbation by hy-

1-Cyclohexyluracil and 9-ethyladenine were obtained from Cyclo Chemical Corp. 9-*n*-Octadecyladenine was synthesized according to Davoll and Lowy's synthesis of adenosine,[6] using *n*-octadecyl bromide in place of their bromoribose derivative. For 1-*n*-octadecyluracil, the synthesis of 1-methyluracil by Hilbert and Johnson[7] was followed, using *n*-octadecyl bromide in place of methyl iodide. Chloroform was treated with sulfuric acid, followed by alkali and water, and distilled from P_2O_5. Short-path cells (0.033 mm) were used in a Beckman DK-2A spectrophotometer, and solutions of comparable concentration were examined in the infrared (Perkin-Elmer 237 grating instrument) in 1-mm and 1-cm paths, taking advantage of a good window in solvent and silica cells in the range 3500–3150 cm^{-1}. It has been shown[8-10] that 1:1 A···U pairing occurs at high concentration through hydrogen bonding. From our infrared spectra of the A and U derivatives and their mixtures we can, since we are able to observe the nonbonded form, derive the composition of an A + U solution, in terms of the two monomeric and three dimeric species. A···U pairs are favored relative to the homodimers.

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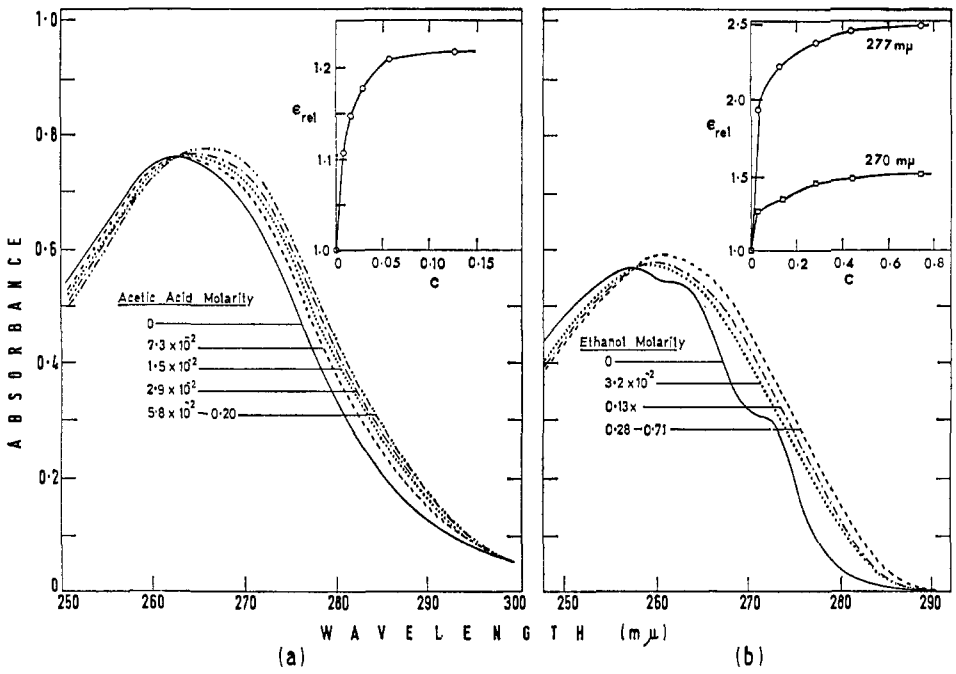

Figure 2. Effect of hydrogen bonding on the absorption spectrum of 9-ethyladenine. (a) Solvent, chloroform; perturbant, acetic acid; (b) solvent, isooctane; perturbant, ethanol. Insets show change of molar absorptivity, relative to the unperturbed value, with molar concentration of added hydrogen-bonding agent. The concentrations of adenine are approximately 8×10^{-5} and 6×10^{-5} *M*.

drogen-bonding agents. In A, however, there is a strong effect. Figure 2 shows the effect of hydrogen bonding to acetic acid in chloroform solution and to ethanol in isooctane. An absorbance increase, as well as a red shift, is noted. Calculations of association constants are precluded by the dimerization of the added hydrogen-bonding agent. However, the insets (Figure 2) show that this change is substantially complete at a perturbant concentration of *ca.* 3% and is not therefore a solvent effect. The hydrogen-bonding acceptor, dioxane, gives much lower association for similar concentrations. Absorbance increases on hydrogen bonding are common,[11,12] though the opposite effect is also known.[11] It may be noted that the two important transitions in the purine base absorption band, suggested[13] to be derived from the benzenoid $A_{1g} \rightarrow B_{2u}$ and $A_{1g} \rightarrow B_{1u}$ bands, undergo an approximately parallel change on addition of solvent (*cf.* ref 11). The possibility that the hypochromic effect is merely a hydrogen-bonding phenomenon, resulting from increased interaction of the π orbitals with nonbonding orbitals in the hydrogen-bonding substituent groups, appears to be excluded by the results of Figure 2. The examination of nuclear magnetic resonance spectra of similar systems[14] appears to exclude any question of base stacking in such solvents.

It is important to note that the A···U pairing need not be of Watson–Crick type, but may instead follow the Hoogsteen scheme;[15] indeed, in mixed A + T crystals this is the form which occurs.[15] From the two types of pairing, for reasonable transition moment directions,[2] it is qualitatively obvious that resonance interaction (corresponding transitions) should be greater in the Watson–Crick form. We are unable to comment categorically on the relevance of these observations to helical nucleic acids in aqueous solution, but a "horizontal" contribution to the hypochromic effect may be envisaged as a possibility under some circumstances.[16]

Acknowledgment. We thank Miss L. Lewis for help with the syntheses, and Professor Sir John Randall for facilities.

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The Formation of Polyenic Dialdehydes in the Photooxidation of Pure Liquid Benzene

Sir:

While the radiolysis and photolysis of aqueous benzene solutions in the presence and absence of oxygen have been studied in detail, particularly by Stein and Weiss[1a-f] and Dorfman, *et al.*,[1g] the photooxidation of dry liquid benzene has not been reported.[2] We have

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