which develops to *full* color intensity in a few hours, the half-life being 43 ± 5 min. Exposure to the PEK lamp with a 3500-A cut-off filter for a period of 10 sec results in complete bleaching, the original color being restored in the dark with a half-life of 41 ± 5 min (with apparent color re-formation beginning almost immediately).[8]

It is necessary to demonstrate that the red, stable form on silica gel was indeed the same species as the open, unstable, blue photochromic species in solution. It is known that adsorption produces electronic spectral shifts, so the fact that one colored form is red to the eye while the other is blue is not surprising (in fact, the recorded visible spectra are quite similar as indicated in Figure 1; *vide infra*). Two experiments have demonstrated that these are the same species.[9] (1) Elution of bright red IB from a silica gel chromatography column with methanol yielded a deep blue solution with a visible spectrum identical with that of IB produced photochemically in methanol. The blue eluent bleached in the dark after 1 hr. (2) Addition of silica gel to blue IB produced photochemically in cyclohexane yielded immediately the red IB with substantial color development; *i.e.*, the visible optical density was equivalent to that attained after 20 min from the time of adding silica gel to an initially colorless solution of IA in cyclohexane in the dark.

That the photobleached material is the spiropyran is indicated by the identity of the half-lives for color formation in a cyclohexane solution of the spiropyran upon adsorbing it onto silica gel and by color re-formation in a photobleached sample on silica gel.

Ultraviolet and visible spectra of IA in cyclohexane and IB in cyclohexane–silica gel and in methanol are given in Figure 1. The blue shift in the S_1 transition and red shift in the S_2 transition in IB in going from methanol to the silica matrix are not unreasonable with respect to magnitude,[1] but we make no attempt to rationalize them with respect to direction since the respective transitions have not been assigned.

The observations reported in this communication are in accord with the following simple mechanistic view. In solution, even in polar solvents, the most stable tautomer of I is IA which may, however, be photochemically converted to relatively unstable IB with quantum yield on the order of 0.1–0.01.[4] On highly polar, partially hydrated silica gel, the open, polar IB is stable relative to IA, to which it may be photoconverted with quantum efficiency qualitatively of similar magnitude. The "driving force" of either photoconversion is maintained simply by the relative extinctions of the two tautomers at the exciting wavelengths.[10]

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(8) All irradiations were carried out in 0.1-cm path-length quartz cells, which were also used directly for visible and ultraviolet spectral analyses.

(9) We do not mean to imply that the red species on silica gel and the blue species in solution are necessarily the same mixture of geometrical isomers of IB (see ref 4).

(10) This discussion is essentially in agreement with that pertaining to a related system, 1,3,3-trimethylindolino-6′-nitro-8′-methoxybenzopyrylospiran adsorbed on silicic acid, which has been the subject of a very recent preliminary report by C. Balny and P. Douzou, *Compt. Rend.*, C264, 477 (1967). We thank a referee for bringing this to our attention.

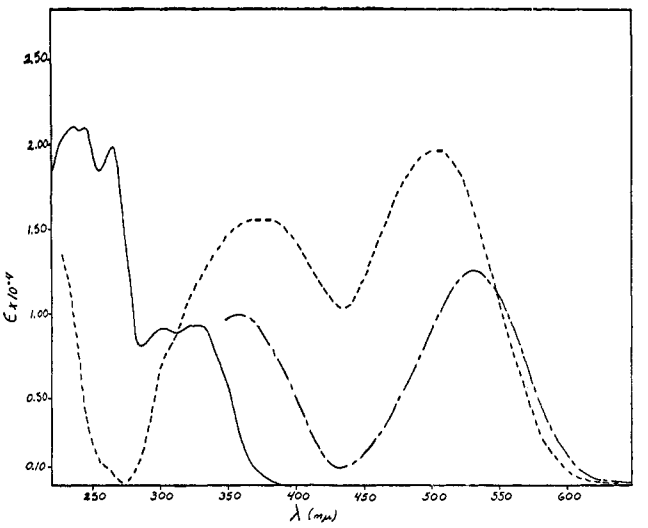

Figure 1. Ultraviolet and visible spectra of IA and IB: ——, IA in silica gel–cyclohexane; - - - - -, IB in cyclohexane; — - — -, IB in methanol.

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Spectroscopy and Photochemistry of *all-trans*-Retinal and 11-*cis*-Retinal

Sir:

Because of the important role of 11-*cis*- and *all-trans*-retinals in the visual process,[1-3] we wish to report several new results relative to their spectral and photochemical behavior.

While the absorption spectra[4,5] at different temperatures and nmr spectra[6,7] of these isomers have been reported, the low-temperature emission spectra and excitation spectra have not appeared.

Irradiation of any of the isomers in alcohol solution at room temperature is said to produce a photostationary equilibrium with the *all-trans* isomer as the predominant isomer.[8] *all-trans*-Retinal at 77°K showed some unknown reversible photochemical behavior as determined by monitoring intensity changes of the long-wavelength absorption band.

all-trans-Retinal was obtained from Sigma Biochemicals and recrystallized twice from 95% ethanol. The 11-*cis*-retinal was a gift from Hofmann-La Roche Co. and had been purified by them. In addition, nmr spec-

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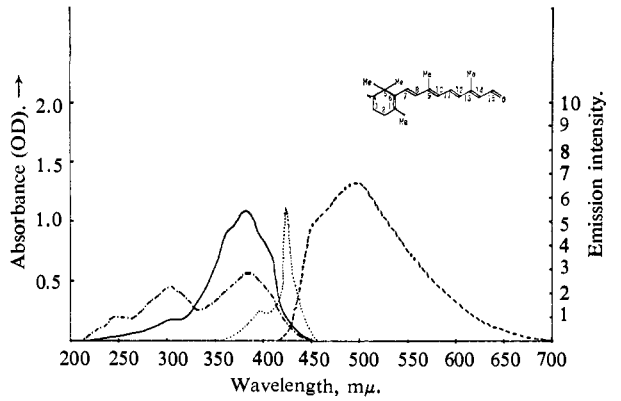

Figure 1. Absorption (——), emission (- - - -), fluorescence excitation (· · · ·), and absorption after 2.5-hr irradiation (—·—·—) of *all-trans*-retinal at 77°K.

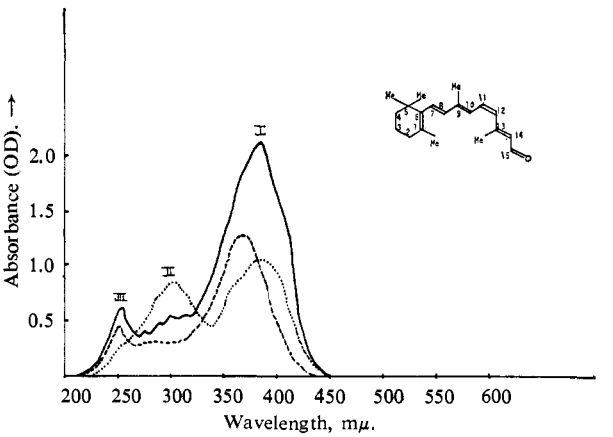

Figure 2. Absorption at 77°K (——), room temperature (- - - -), and 77°K after 0.5-hr irradiation (· · · ·) of 11-*cis*-retinal.

tra and thin-layer chromatography on silica gel in our laboratories showed no impurities for either isomer. Except where noted, all spectra were run in highly purified and dried 3-methylpentane (3-MeP) and at 77°K. All solutions were carefully vacuum degassed by multiple freeze–thaw cycling. The absorption spectra were run on a Cary 15 spectrophotometer while the emission and excitation spectra were obtained by front-face illumination. All concentrations were approximately 10^{-4} *M*.

all-trans-**Retinal**. Figure 1 illustrates typical low-temperature absorption, emission, and excitation spectra of *all-trans*-retinal. Both the long-wavelength absorption band and emission spectrum have Franck–Condon forbidden shapes. The shoulders are somewhat more defined at 77°K than at 300°K. The long-wavelength transition is assigned $^1B \leftarrow {}^1A$ according to the nomenclature of Platt.[9]

The emission is assigned as a fluorescence since it overlaps the long-wavelength tail of the absorption and is a mirror image of the Franck–Condon forbidden shape of the absorption. Further, the emission does not pass through a phosphoroscope having a resolving time of 5×10^{-4} sec. These spectra are similar in EPA (ether–isopentane–ethanol, 5:5:2) at 77°K. The shoulder on the short-wavelength side of the emission apparently arises from a photoproduct. The room-temperature fluorescence, while weaker than at 77°K, is shaped similar to the low-temperature emission.

The excitation spectra exhibits the unusual characteristic of maximizing in a region which is near the onset of absorption. This fact indicates the intensity of emission is at its maximum near the onset of absorption and, further, decreases at shorter wavelengths as the intensity of absorption increases (Figure 1). Similar results have been obtained by Becker, *et al.*,[10] on other molecules capable of undergoing photochemistry. Although more details will appear elsewhere, this effect results from competitive photochemistry (relative to internal conversion) at higher vibronic levels of the first excited state. Further, the two sharp band maxima in the excitation spectrum very likely are the location of the unresolved 0–0 band and poorly resolved 0–1 band in absorption.

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11-*cis*-Retinal. Figure 2 shows a typical low-temperature absorption spectrum of 11-*cis*-retinal. The three electronic bands have been enumerated I, II, and III for reference purposes only. We assign $^1B \leftarrow {}^1A$ to transition I and $^1C \leftarrow {}^1A$ to transition III. Transition II remains unassigned.

The initial emission intensity of 11-*cis*-retinal at 77°K is very weak, 10% of *all-trans*-retinal emission, and, in fact, does not seem to appear until the sample has been irradiated by the exciting light (424 or 383 mμ) for 3–5 min. Thereafter, the emission continues to increase, but at all times the emission and excitation spectra are essentially identical with those of *all-trans* retinal. Therefore, we conclude that 11-*cis*-retinal probably does not fluoresce and the weak emission that is observed is from photoproduced *all-trans*-retinal.

Irradiation into the band at ~380 mμ through Corning filter No. 5562 for *all-trans*-retinal and through Corning filter No. 5543 for 11-*cis*-retinal at room temperature and 195°K in fluid solution results in irreversible photochemistry. That is, the band begins an immediate and continued reduction in intensity until it is decreased by 75% within 5 min. Warming from 195°K to room temperature does not increase the intensity. However, at 77°K both of these isomers undergo reversible photochemistry. Irradiation into the long-wavelength band of either isomer with the same filters as above produces a vibrationally structured band with a maximum at 300 mμ. In the case of the 11-*cis*-retinal this band appears to be an enhancement of band II, Figures 1 and 2. The 13-*cis* isomer shows a similar behavior. Irradiation at 300 mμ as well as warming to room temperature and cooling to 77°K results in the return of the original absorption spectrum, ~95% reversible. We also find a broad structureless emission from the photoproduct maximizing at approximately 460 mμ when excitation is at 300 mμ. Monitoring the emission at 460 mμ yields an excitation spectrum with a peak at 335 mμ. Although we can speculate regarding the nature of these photoreactions, further effort is required to elucidate fully their origin.

Additional work is in progress on these two isomers as well as on 9-*cis*- and 13-*cis*-retinals.

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