

Figure 1. Model of the molecule tetrabenzyltitanium in the crystal-line state.

stepwise introduction of the C atoms into the structure factor calculations, their location being derived both on Fourier and on stereochemical grounds. Least-squares refinement was carried out in 16 cycles which were alternately of the block-diagonal and of the full matrix type. Only the Ti atom was assigned anisotropic thermal parameters. The final disagreement factor ($R = \sum ||F_c| - |F_o|| / \sum |F_o|$) is 0.128 for the 703 nonzero reflections and 0.176 for all the 1137 reflections subjected to intensity measurement.

The molecular model is shown in Figure 1, while some of the most relevant interatomic distances and bond angles are reported in Table I together with their

Table I. The Most Relevant Geometric Parameters of the Molecule Tetrabenzyltitanium in the Crystalline State^a

Interatomic distances, Å		Bond angles, deg	
Ti-C ₁	2.13 (3)	C ₁ -Ti-C ₈	123 (1)
Ti-C ₈	2.13 (3)	C ₁ -Ti-C ₁₅	118 (2)
Ti-C ₁₅	2.15 (3)	C ₁ -Ti-C ₂₂	102 (1)
Ti-C ₂₂	2.14 (3)	C ₈ -Ti-C ₁₅	106 (1)
Ti-C ₂	2.61 (3)	C ₈ -Ti-C ₂₂	100 (1)
Ti-C ₉	3.16 (3)	C ₁₅ -Ti-C ₂₂	107 (1)
Ti-C ₁₆	2.81 (3)	Ti-C ₁ -C ₂	88 (2)
Ti-C ₂₃	2.95 (3)	Ti-C ₈ -C ₉	116 (2)
		Ti-C ₁₅ -C ₁₆	98 (2)
		Ti-C ₂₂ -C ₂₃	108 (2)

^a The corresponding esd's are given in units of the last significant digit.

standard deviations. All C-C bond lengths and C-C-C angles are close to the average values found in other compounds containing similar groups, the difference never being larger than 3σ (average values $\sigma_{C-C} = 0.04$ Å, $\sigma_{C-C-C} = 2^\circ$). Although the largest distance of the C atoms from the least-squares average planes of their corresponding benzyl groups is 0.07 Å, we do not believe that any deviation from planarity may be claimed. The most interesting structural feature is the apparent existence of Ti-C electronic interactions with the benzyl C atoms in the β position; this is

revealed by short Ti-C distances especially with C₂ and C₁₆ (in the range 2.6–2.8 Å; see Table I), together with Ti-C _{α} -C _{β} angles well below the tetrahedral value, and with a rotational orientation of the phenyl ring bringing the C _{β} π -electron clouds as close as possible to the metal. The last is a common feature of the four benzyl groups, since all dihedral angles between the phenyl rings and the Ti-C _{α} -C _{β} plane are between 84 and 86°, suggesting that there is probably some degree of overlap between the C _{β} filled π orbitals and the outer-shell Ti empty orbitals. The carbon-to-metal electron donation may explain the shift to lower field of the C _{α} proton resonance in the high-resolution nmr spectra of I, with respect to the benzyl derivatives of metals with a similar or higher electronegativity,³ due to electron draining from C _{α} to C _{β} . The Ti-C _{β} interactions, together with steric repulsions between non-bonded atoms, offer a good qualitative explanation of the observed deviations of the C _{α} -Ti-C _{β} angles from the tetrahedral value. In particular (see Table I and Figure 1), the largest angle is observed for C₁-Ti-C₈ (123°), consistent with the C₂-C₁-Ti-C₈ sequence being in a cis arrangement and with C₂ being the C _{β} atom closest to Ti. Furthermore, C₁-Ti-C₁₅ is the second largest angle (118°), consistent with C₂ and C₁₆, bonded to C₁ and C₁₅, respectively, being the two C _{β} 's closest to Ti.

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The Hydrogen-Bonded (Protonated) Schiff Base of *all-trans*-Retinal¹

Sir:

As a part of our continuing investigation of the visual pigments,^{2,3} we have studied a Schiff base of *all-trans*-retinal. We have obtained a unique result which directly bears upon all previous reports correlating an absorption band to the so-called protonated species. In particular, we have been concerned with the effect of temperature and of a hydrogen bonding (protonating) species upon the *N-all-trans*-retinylidene-*n*-butylamine molecule. The latter is considered to be a model for prelumirhodopsin (*all-trans*-retinal opsin), the first intermediate in the photobleaching of rhodopsin.

Preparation of the imine was similar to that previously reported.⁴ Absorption spectra were recorded on a Cary-15 spectrophotometer. Infrared spectra were

(1) This research was supported by the Atomic Energy Commission, Grant No. ORO-3736-8.

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recorded on a Beckman IR-10. The solvent for all experiments was 3-methylpentane, where not specified.

The room temperature spectrum of the all-trans Schiff's base is similar to that previously reported,⁴ λ_{\max} 356 nm. When cooled to 77°K, the absorption maximum is red shifted to 364 nm. Room temperature addition of HCl gas forms a pale yellow solution having an absorption, λ_{\max} 435 nm. Cooling this solution (after 5 min at room temperature) to 77°K shifts the absorption maximum to 440 nm. However, if the solution is immediately cooled after addition of HCl, a peak can be detected at 542 nm with the main peak shifted to \sim 460 nm; see Figure 1. When this solution is warmed to 97°K, we observe the growth of the 542-nm peak as well as a 318-nm peak and the simultaneous decrease in the 460-nm peak. Furthermore, at this temperature (97°K) an isosbestic point appears at 486 nm and the 542-nm (and 318-nm) maximum will continue to grow if this temperature is maintained. The 542-nm band can be observed at temperatures as high as 143°K. Above the latter temperature, the absorption spectrum is identical with that measured at room temperature (λ_{\max} 435 nm) and recooling to 77°K again produces a red shift to 440 nm. No regeneration of the 542-nm maximum is observed when the solution is warmed to temperatures above 150°K (but is reversible at lower temperatures).

No concentration dependence of the foregoing phenomena is observed in the range 10^{-4} – 10^{-5} M. Moreover, it should be pointed out that a solution initially exhibiting no shoulder at 542 nm can be allowed to set at \sim 100°K and the 542-nm band will be generated.

Irradiation (500-W Hg–Xe lamp) of any of the foregoing solutions for 30 min produces no change in the absorption spectrum except for the room temperature Schiff's base where a decrease in the intensity of the first transition and increase in the intensity in the 250-nm region results. This behavior is interpreted as resulting from a trans–cis isomerization.^{3,5}

The imine in chloroform has an absorption maximum at 364 nm at ambient temperatures. Addition of anhydrous HCl gas turns the solution brown and shifts the maximum to 462 nm, in good agreement with work done on the ethanolamine Schiff base.⁶ The ir spectra of the two chloroform solutions were essentially identical, indicating no change in the imine structure. Other ir spectra (Nujol and KBr) show two peaks (1620 and 1660 cm^{-1}) for the basic form. After acidification by directly passing HCl gas over the Nujol or KBr sample, the peak at 1620 cm^{-1} disappears and the 1660- cm^{-1} peak becomes more intense. It is obvious that the same phenomenon is not occurring in the chloroform solution and in the solid state.

Previous attempts have been made to explain the differences in the wavelength of the transition with a maximum at \sim 440 nm. These include, for example, shifting as a function of solvent polarizability⁷ (using a perchlorate salt of retinal condensed with pyrrolidine) or the degree of inductive effect of substituents at the meta and para positions of aniline condensed with retinal.⁸

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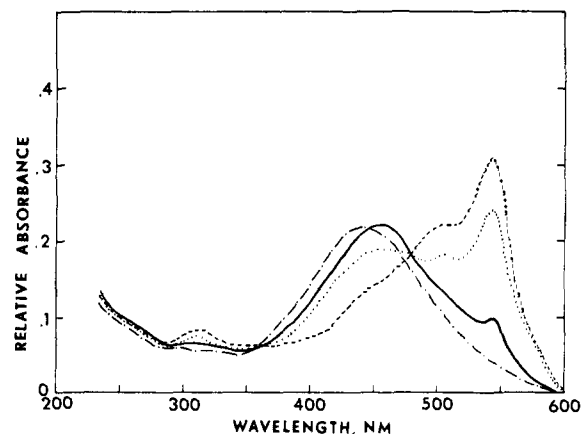


Figure 1. Absorption spectra of *N*-all-trans-retinylidene-*n*-butylamine + HCl in 3-MP cooled immediately to 77°K (—); warmed to 97°K (....); temperature held constant at 97°K (---). Spectra of the all-trans Schiff base + HCl after 5 min at room temperature then cooled to 77°K (-.-.-).

From our low-temperature data, it seems reasonable that the rapid cooling of the protonated Schiff's base to 77°K produces a nonequilibrium mixture of the HCl in the rigid matrix. Also, the HCl is more concentrated than that at ambient temperatures. One conclusion consistent with the data reported here is that the absorption spectrum of the Schiff's base is shifted to longer wavelengths essentially because of the existence of the polar HCl molecules in a solvent cage. However, in addition we have observed spectral bands that have not been previously reported. It is apparent that the degree of HCl interaction must play an important role. Since the solvent cage containing HCl results in an absorption at 440 nm (77°K) the absorption spectrum recorded at 97°K must represent some definitive species that has maxima at 542 and 318 nm. We believe that this is the true hydrogen-bonded (protonated) species. The existence of the isosbestic point is further evidence for this conclusion. The two species in equilibrium would be the Schiff's base in a solvent cage and the hydrogen-bonded complex. Low temperatures favor the hydrogen-bonded species, but at certain higher temperatures (*vide supra*) this species is not observed. This is a consequence of the comparative hydrogen-bond energy and the magnitude of the kT energies.

From the data reported here, we conclude that the long-wavelength absorption maximum of the hydrogen-bonded (protonated) Schiff's base is 542 nm. It is clearly worth pointing out that the location of the absorption maximum is essentially identical with that of prelumirhodopsin, λ_{\max} 543 nm.⁹ Similar studies are in progress on the *n*-butylamine Schiff bases of the mono-cis isomers of the retinals and will be reported in the future.

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