

Figure 1. Rhodopsin kinase assay of hexane-washed bovine opsin and pigments. Curve 1: 1-rhodopsin (hexane washed). Curve 2: Opsin (hexane washed). Curve 3: Rhodopsin (hexane washed). Curve 4: Retinal-free opsin treated with 11-*cis*-retinal (no further hexane wash).

intermediate Regenerated from Native 11-*cis*-Retinal and 11-*Cis*-Locked 1. The difference spectra (Nicolet 7199, 256 scans with full aperture, mirror velocity 45 cm/s, resolution 2 cm⁻¹ at room temperature) were measured with films deposited on a ZnS window with samples prepared as described earlier.¹⁸ The meta II stage was obtained by 250-W irradiation through a 500-nm filter, 1 min, 24 °C, its formation being checked by characteristic changes in carboxylic acid peaks in the difference FTIR spectra,¹⁹ and visible absorption spectra of hydrated films on quartz. The difference spectrum of *native* red outer segment and meta II matched published data,¹⁹ but that of pigment regenerated from 11-*cis*-retinal showed additional peaks at 1203 and 950 cm⁻¹ arising from the meta I intermediate²⁰ (Figure 2); the difference

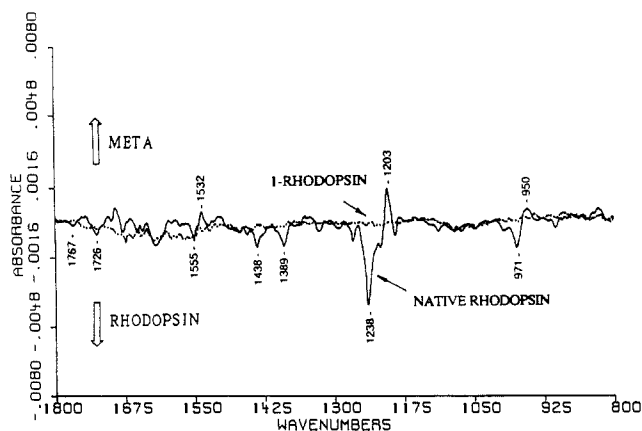


Figure 2. Solid curve: Difference FTIR spectrum between meta-rhodopsin II (shown as positive peaks) and rhodopsin (shown as negative peaks) in rhodopsin regenerated from hexane-washed bovine opsin and 11-*cis*-retinal. Dotted curve: Difference FTIR spectrum between meta-rhodopsin II and rhodopsin in 1-rhodopsin regenerated from hexane-washed bovine opsin and retinal analogue 1.

visible spectrum also showed the presence of meta I as a 490-nm shoulder on the main 380-nm meta II peak. No change is seen in the difference spectrum between 1-rhodopsin and the corresponding "meta II" (Figure 2). Thus, despite the sensitivity of the FTIR difference technique which can detect single protonation/deprotonation changes,^{18,19} 1-rhodopsin shows changes in neither the protein nor the chromophore moieties.

The RK and FTIR results corroborate the lack of light dependency seen in the partial restoration of sensitivity by analogue 1 in the bleached salamander rods. However, these results do not parallel those in the *Chlamydomonas* assay, in which 1 restored phototactic ability in a light-dependent manner.⁸ Studies on the bovine, salamander, and *Chlamydomonas* systems are ongoing.

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(17) Phosphodiesterase assays on the analogue pigments indicated some activity which was less than that observed for rhodopsin. However, inability to establish an opsin blank for these experiments prevents us from making any conclusions.

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(19) (a) Siebert, F.; Mantele, W.; Gerwert, K. *Eur. J. Biochem.* **1983**, *136*, 119–127. Rothschild, K.; Cantore, W. A.; Marrero, H. *Science* **1983**, *1333*–1334. (b) de Grip, W.; Gray, D.; Gillespie, J.; Bovee, P. H. M.; van den Berg, E. M. M.; Lugtenberg, J.; Rothschild, K. *Photochem. Photobiol.* **1988**, *48*, 497–504.

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Additions and Corrections

Electrically Conductive Metallomacrocyclic Assemblies. High-Resolution Solid-State NMR Spectroscopy as a Probe of Local Architecture and Electronic Structure in Phthalocyanine Molecular and Macromolecular "Metals" [*J. Am. Chem. Soc.* **1986**, *108*, 437–444]. PAUL J. TOSCANO and TOBIN J. MARKS*

Page 443: The negative sign in eq 1 should be moved from the rightmost to the middle term and the signs of the a_i values in Table II adjusted appropriately. This typographical error in no way affects the key conclusions of this work.

Experimental and Theoretical Evidence for Nonlinear Coordination of "sp-Hybridized" Carbon Atoms: The Gas-Phase Structure of Trifluoroethylidyne-sulfur Trifluoride, CF₃-C≡SF₃ [*J. Am. Chem. Soc.* **1987**, *109*, 4009–4018]. DINES CHRISTEN, HANS-GEORG MACK, COLIN J. MARSDEN,* HEINZ OBERHAMMER,* GABRIELE SCHATTE, KONRAD SEPELT, and HELGE WILLNER

The bending angles [$\theta = 180 - \text{CCS}$] given in the theoretical calculations for CF₃-C≡SF₃ in Table VIII and in Figure 6 (p 4016) are too large by a factor of 2. Similarly, the calculated energy minima in the Note Added in Proof should read as follows: 180° (HF), 162° (MP3), 160° (MP4SD), and 155° (MP4SDQ). Additional calculations with a larger basis set (MP2/6-31G*/HF/6-31G*) result in an energy minimum at C—C≡S = 148°

and in a barrier to linearity of 1.5 kJ/mol corresponding to a thermal average of $\langle \text{C—C}\equiv\text{S} \rangle = 153^\circ$. This theoretical prediction is in good agreement with the electron diffraction experiment, which resulted in $\langle \text{C—C}\equiv\text{S} \rangle = 155(3)^\circ$ and in an estimated barrier of ≥ 2.0 kJ/mol.

Stereoselective Syntheses of the Nonactate Esters via Intramolecular Oxymercurations of Allenes [*J. Am. Chem. Soc.* **1990**, *112*, 1597]. ROBERT D. WALKUP* and GYOOSUN PARK

Our assertion that no previous syntheses of homononactate acid had been reported was incorrect, as we overlooked the first total syntheses of (+)- and (-)-methyl homononactate, as well as their utilization in the first total synthesis of tetranactin, by Schmidt and Werner: Schmidt, U.; Werner, J. *J. Chem. Soc., Chem. Commun.* **1986**, 996–998. Schmidt, U.; Werner, J. *Synthesis* **1986**, 986–992.

In addition, our discussion of the trends observed for the NMR spectra of the syn and anti diastereomers of our 1,3-diol intermediates **18–21** should have referenced the contributions of Hoffmann and Weidmann to this area of stereochemical analysis: Hoffmann, R. W.; Weidmann, U. *Chem. Ber.* **1985**, *118*, 3980–3992.