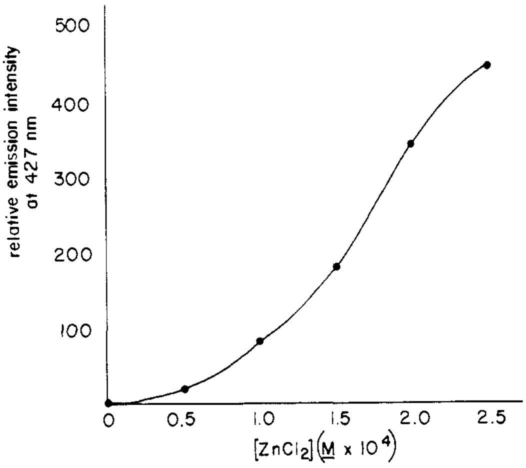

Figure 3. Fluorescence emission intensity of 10^{-4} M compound **1** in acetonitrile as a function of added $ZnCl_2$.

and as seen in entries 4–9 the fluorescence of 9,10-dimethylanthracene is quenched by addition of TMEDA. At [DMA] = 0.1 mM, 4000 equiv of added TMEDA result in quenching by a factor of 80; the intramolecular quenching at the same concentration of compound **1** with no added TMEDA is roughly 30-times more efficient[10] than even this.

Consequently, we explain the observed CHEF in 9,10-bis(TMEDA)anthracene by noting that, when chelated to a metal ion, the amine lone pairs become involved in bonding and are unable to donate an electron to the excited state of the anthracene. This explanation, which has been suggested previously,[7d,e] is corroborated by the pH profile shown in entries 10–15 of Table I (shown graphically in Figure 2) obtained in aqueous solution. At pH 11.7, the amine groups are almost completely unprotonated and the fluorescence of compound **1** is very low; at pH 1.6, most of the amines are protonated, and the fluorescence increases by a factor of over 300. Entries 16–20 indicate that in acetonitrile, the fluorescence increase may be titrated by addition of metal ion (Figure 3).[11] Solubility limits prevent us from further raising the metal ion concentration and therefore determining an asymptotic "intrinsic fluorescence" for complex **2**, which is partially dissociated even in acetonitrile saturated with $ZnCl_2$ (entry 20). The same titration done in aqueous solution fails; it is not surprising that the complexation of zinc ion with **1** in water is not complete at equimolar concentrations. Cryptands leading to polydentate chelation will provide much larger association constants.

These results predict that nitrogen-containing ligands with known specificities for metal ions may be utilized as fluorescent probes via a simple, flexible connection to a fluorescent compound such as anthracene. Complexation need not change the conformation of the fluorophore, as required by an "inhibition of vibrational decay" mechanism, but it must tie up amine lone pairs. Indeed, it may be possible to tie up amine lone pairs in other interesting ways, such as ion-pairing or strong hydrogen bonding; each interaction suggests potential analytical applications. Furthermore, the great distance through which electron transfer may occur suggests that amine and fluorophore groups need not be proximal to one another. We believe this approach to the design of fluorescent analytical probes has considerable potential and are continuing our work on this topic.

Acknowledgment. We gratefully acknowledge support for this work from the National Science Foundation and from The Ohio State University in the form of a graduate fellowship to one of us (M.E.H.). Shared resources, including the use of a fluorimeter, were made available by Prof. M. Platz of this department. FT NMR spectra were obtained with equipment funded in part by NIH Grant No. 1 S10 RR01458-01A1. We are particularly appreciative for the highly constructive suggestions of several reviewers.

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[10] Comparing the relative intensity of 9,10-bis(TMEDA)anthracene (entry 3) with that of 9,10-dimethylanthracene plus 4000 equiv of TMEDA (entry 9).

[11] The emission intensity of **1** plus 2 equiv of $ZnCl_2$ is less than that of preformed **2**. We attribute this primarily to the fact that $ZnCl_2$ is hygroscopic; hydration will increase its apparent molecular weight and thereby decrease the actual concentration of added zinc. Binuclear complex **2** has been shown to be anhydrous by microanalysis (cf. ref 3); this is expected inasmuch as TMEDA complexation is known to provide a source of anhydrous zinc chloride (Isobe, M.; Kondo, S.; Nagasawa, N.; Goto, T. *Chem. Lett.* **1977**, 679). While the CHEF of a different complex is reported to be diminished by the addition of water to the acetonitrile solution (cf. ref 7f), we observe a small (15%) increase upon addition of 1 × 10^{-2} M water to the solution described in entry 2, Table I.

Electrocyclic Reactions of 13-*cis*-Retinal Schiff Bases

William H. Okamura,* Angel R. de Lera, and
Wolfgang Reischl

Department of Chemistry
University of California, Riverside
Riverside, California 92521

Received March 17, 1988

Bacteriorhodopsin, the protein that functions as a photochemical proton pump coupled to ATP synthesis in the purple membrane of Halobacterium halobium, consists of retinal bound to a lysine residue via a Schiff base linkage.[1] Protonation–deprotonation of the retinal Schiff base nitrogen and cis–trans isomerization of its Δ^{13} double bond are considered to be intimately involved in the proton pump photocycle.[2] As a spectroscopic model for bacteriorhodopsin, Schiff base derivatives of *all-trans*-retinal (**1a**) and 13-*cis*-retinal (**2a**) have been studied extensively, especially in terms of their electronic and vibrational absorption characteristics.[3] Synthetic investigations in this laboratory have allowed access to a variety of side chain analogues[4a–c] of retinal, and we have accordingly initiated a systematic investigation of the chemical and spectroscopic properties of the corresponding Schiff bases, in both their protonated and deprotonated forms. It is the purpose of this communication to report the extraordinarily facile six-electron electrocyclization[5] of Schiff bases of 13-*cis*-retinal

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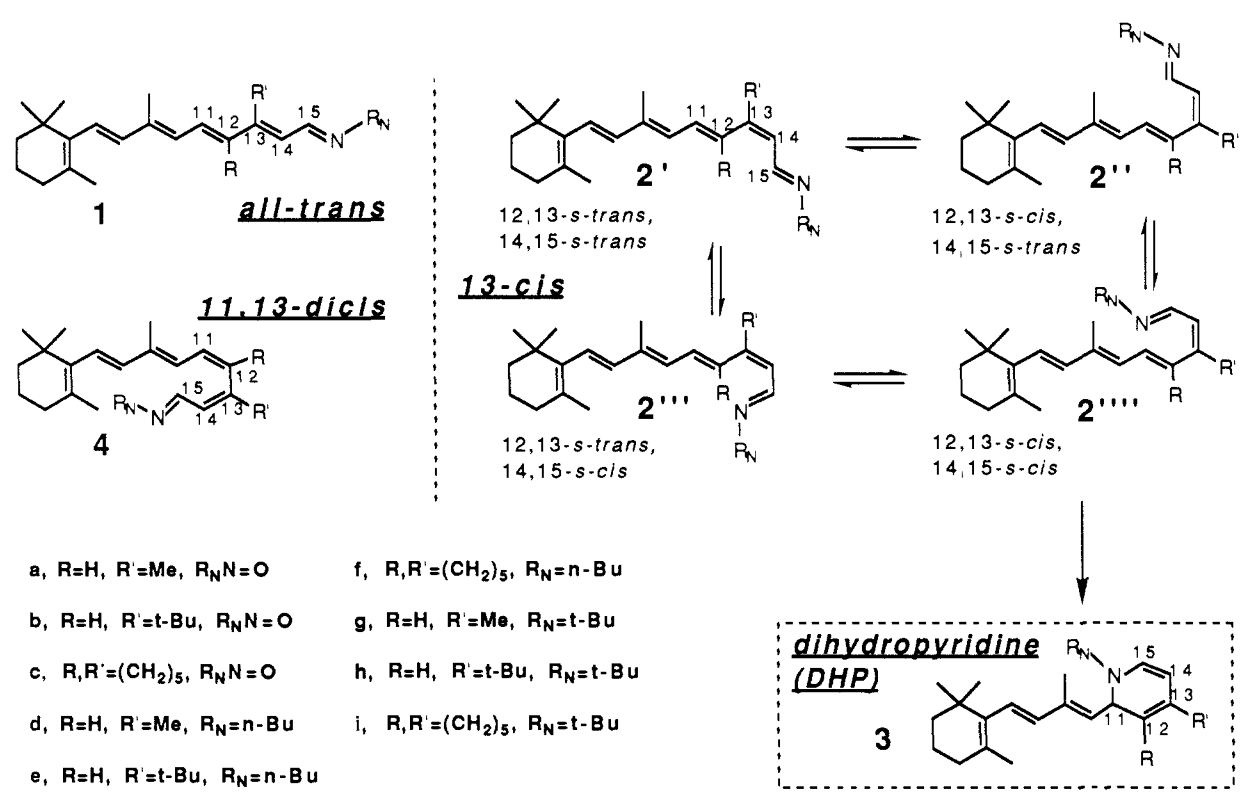

a, R=H, R'=Me, R_NN=O

b, R=H, R'=t-Bu, R_NN=O

c, R,R'=$(CH_2)_5$, R_NN=O

d, R=H, R'=Me, R_N=n-Bu

e, R=H, R'=t-Bu, R_N=n-Bu

f, R,R'=$(CH_2)_5$, R_N=n-Bu

g, R=H, R'=Me, R_N=t-Bu

h, R=H, R'=t-Bu, R_N=t-Bu

i, R,R'=$(CH_2)_5$, R_N=t-Bu

Figure 1.

analogues to 1,2-dihydropyridines (**3**, DHP) and to report that this process is also characteristic to a significant degree of the parent system as well.

Using a standard procedure for the preparation of retinal Schiff bases, 13-*tert*-butyl-13-*cis*-retinal (**2b**)[4a,d] reacted with *n*-butylamine (anhydrous ethanol, 4A molecular sieves, 1 h at 0 °C, 1 h at room temperature)[2a,3k-m,6] to afford not the expected Schiff base **2e** but rather the six-electron electrocyclized DHP **3e** (^{1}H NMR, 300 MHz; in C_6D_6 or $CDCl_3$).[7] This cyclized material could be recovered essentially unchanged (^{1}H NMR) upon heating a sample in C_6D_6 at 78 °C for 14 h.

Although the cyclization of *cis*-dienone oximes to pyridines has been suggested[8] to occur through the intermediacy of dihydropyridines, only *N*-acyl-1,2-dihydropyridines have been isolated by electrocyclic ring closure of *N*-acyl-azatrienes,[9] but only by flash vacuum pyrolysis (650 °C) of triene precursors. The mild conditions (2 h, ≤room temperature) needed to effect the cyclization of **2e** to the DHP **3e** are accounted for on the basis that it exists primarily in its 12-*s-cis*-conformation[4a,10] **2''e** and it need undergo only 14-*s-trans* to 14-*s-cis* conformational isomerism (**2''e** to **2''''e**) before electrocyclization. That the formation of cyclized material **3** indeed proceeds through electrocyclization of Schiff base **2** is supported by the observation that *n*-butylamine treatment of 13-*cis*-12-*s-cis*-locked retinal **2c**[4bc,10] affords initially a ~1:1 mixture of Schiff base **2f** and DHP **3f**. Allowing this mixture to stand in C_6D_6 ($\tau_{1/2}$ ~ 70 min, ~23 °C) leads to complete conversion to DHP **3f** (^{1}H NMR).[7]

We have previously shown that the corresponding 11,13-*dicis* aldehydes **4b** and **4c** isomerize to 13-*cis* aldehydes **2b** and **2c**,[4a-c] presumably through the intermediacy of α-dihydropyrans **3b** and **3c**. Freshly purified 13-*tert*-butyl-11,13-*dicis*-retinal **4b**[4a] (accompanied by 8% of the 13-*cis* isomer **2b**[4a,d]), when treated with *n*-butylamine as above, afforded Schiff base **4e** accompanied by 18% of DHP **3e** (^{1}H NMR), which can be considered to be produced from electrocyclization of **4e** as well as from the contaminant of **2b** (8%) already present in **4b**. That in fact cyclization from **4e** to **3e** also occurs (although at a slower rate than the conversion of **2e** to **3e**) was demonstrated by heating the mixture of **4e** and **3e** in C_6D_6 (78 °C, $\tau_{1/2}$ ~ 4 min) leading to pure DHP **3e**. The 12-*s-cis*-locked-11,13-*dicis*-aldehyde **4c** was also exposed to *n*-butylamine to afford the 11,13-*dicis* Schiff base **4f**, which required temperatures higher ($\tau_{1/2}$ ~ 12 min, 78 °C) than did 13-*cis* Schiff base **2f** to cyclize to the same DHP **3f**.[7] The sluggishness with which 11,13-*dicis* Schiff bases (conformations not depicted) electrocyclize to DHP's compared with that of the 13-*cis* isomers is in accord with the view that the greater steric congestion in the former imparted by the presence of a 11-*cis* double bond impedes electrocyclization. Introduction of bulky substituents at the termini of polyenes undergoing electrocyclization generally attenuates the rate of ring closure.[5b-d] Also in accord with this view is the finding that whereas reaction of aldehyde **2b** with *n*-butylamine affords only DHP **3e**, its exposure to *tert*-butylamine affords the corresponding Schiff base **2h** along with ~24% of DHP **3h**. It was also determined that heating this mixture of **2h** and **3h** for 30 min (C_6D_6, 78 °C) or heating **4h** (obtained from **4b** plus *tert*-butylamine) for 95 min under the same conditions afforded the same **2h**/**3h**/**4h** equilibrium mixture (~ 5:3:2), which remained virtually unchanged after 13.5 h at 78 °C. The corresponding 12-*s-cis*-locked-13-*cis*-*tert*-butylamine Schiff

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base **2i**, however, could be formed cleanly without contamination by cyclic material (cf. the preparation of **2f**).

Finally, in the parent system 13-*cis*-**2d**, presumably possessing a predominant 12-*s*-*trans* conformation **2′d**,[3j–l,6] the electrocyclization process is also operating, albeit to a smaller extent. The product obtained upon treatment of 13-*cis*-retinal (**2a**) with *n*-butylamine contains, besides 8% of *all-trans*-retinal Schiff base **1d**, 7% of the corresponding DHP **3d**.[7,11] Upon heating this mixture at 78 °C in C_6D_6 for 30 min, the composition of the mixture changed to a 2:5:3 ratio of 13-*cis*-**2d**, *all-trans*-**1d**, and DHP-**3d**. Further heating led to deterioration. No DHP was observed with *tert*-butylamine, only Δ^{13} isomerization of the Schiff base **2g** (initially accompanied by 7% **1g**) being observed (a mixture containing 13-*cis*-**2g** and *all-trans*-**1g** in a ratio of 3:1 was obtained after heating in C_6D_6 at 78 °C for 30 min).

Thus, in view of the extensive use of Schiff base models in studies of bacteriorhodopsin and related pigments, it is evident then that some caution must be exercised in interpreting electronic and vibrational data of 13-*cis*-retinal Schiff base systems because of possible DHP contamination. The significance if any of the formation of 1,2-dihydropyridines (DHP) or the occurrence of other pericyclic processes to the photocycle of bacteriorhodopsin or other retinal containing pigments[12] is an intriguing question.

Acknowledgment. This study was supported by NIH Grant DK-16595. We also acknowledge NATO for a Postdoctoral Fellowship to A. R. de Lera and Badische-Anilin und Soda Fabrik, Ludwigshafen, for providing starting materials utilized in this study.

Supplementary Material Available: Tables of NMR spectral data and sample preparation (4 pages). Ordering information is given on any current masthead page.

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Photophysics of Metal Complexes of Spheroidal Carbon Shells[†]

F. D. Weiss,[‡] J. L. Elkind, S. C. O'Brien,[§] R. F. Curl, and R. E. Smalley*

Rice Quantum Institute and
Department of Chemistry, Rice University
Houston, Texas 77251

Received January 27, 1988

In the fall of 1985 initial evidence was presented for the formation of a new class of organometallic ions consisting of a single metal atom surrounded by a spheroidal cage network of pure carbon.[1] The new species were made by laser vaporization of a $LaCl_3$ impregnated graphite disc in a pulsed nozzle followed by intense laser ionization of the neutral clusters in a supersonic beam. The most prominent of these species was $C_{60}La^+$. Its exceptionally high photophysical stability led to the suggestion that the La atom had been trapped inside the closed shell of the (putatively) icosahedral carbon cage,[2] C_{60}.

To test this rather controversial[3–5] hypothesis, we have performed extensive photophysical and chemical measurements in the magnetic trap of an FT-ICR mass spectrometer. Initial results are presented here with more extensive experiments and discussion to follow.[6] The details of this cluster beam/FT-ICR apparatus have been presented previously[7] as well as several of its early applications to metal[8,9] and semiconductor[10] cluster surface chemistry. Carbon–metal cluster ions were prepared in the supersonic beam by laser-vaporization of a graphite disk impregnated with a salt of the desired metal (La, K, Cs). After injection into the ICR trap and subsequent thermalization with neon gas,[10] the only clusters observed in the 300–1500 amu mass range were the even-numbered bare carbon clusters, C_n^+, and the same clusters with a single metal atom attached, C_nM^+. Ample evidence has been found for the presence of other, more weakly bound metal–carbon clusters in these beams,[1,6] including some containing more than one metal atom (e.g., $C_nK_2^+$).[4,5] However, these weakly

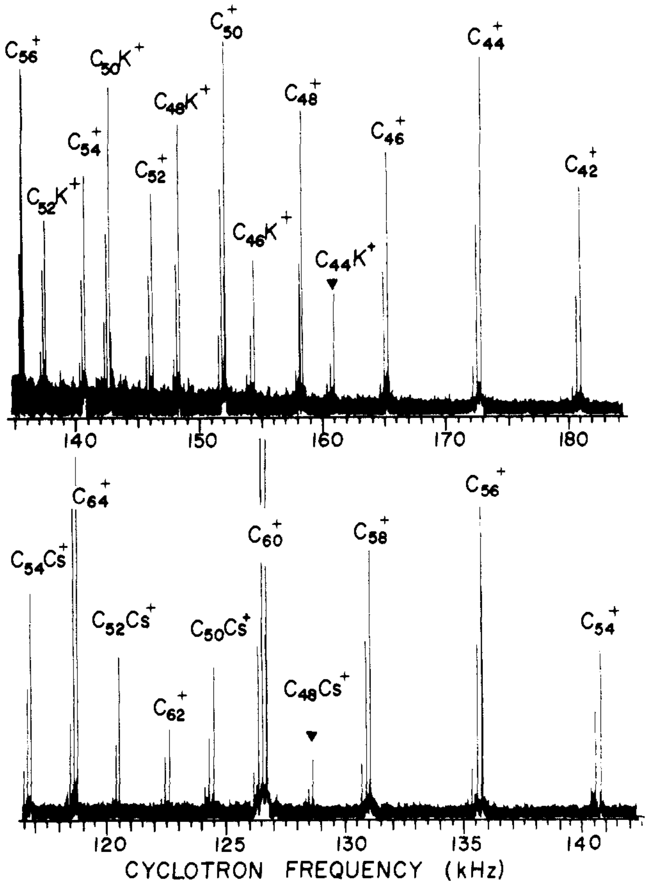

Figure 1. High-order photofragmentation pattern of $C_{60}K^+$ (top) and $C_{60}Cs^+$ (bottom) detected by FT-ICR mass spectrometry. Note the C_nK^+ fragment series breaks off at 44, while the C_nCs^+ series terminates at 48. The bare C_n^+ clusters seen in the top panel are fragments from C_{64}^+ injected into the ICR trap along with $C_{60}K^+$ providing an internal calibration, while in the bottom panel these C_n^+ fragments result from C_{72}^+ parent ions. Conditions (top panel): 200 shots at 10 Hz of ArF excimer laser radiation (193 nm) at 6 mJ cm^{-2} shot^{-1}; (bottom panel): 1600 shots ArF at 3 mJ cm^{-2} shot^{-1}. During laser excitation the pressure in the ICR trap was less than 1 × 10^{-8} Torr. A few noise spikes have been removed to simplify the figure.

[†] Research supported by the National Science Foundation and the Robert A. Welch Foundation.

[‡] Department of Physics, Rice University.

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