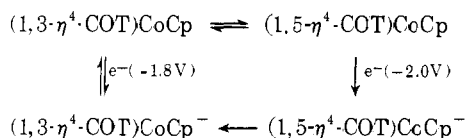


NMR spectroscopy allows identification of **B** as the 1,5-bonded diene **2**, as previously reported by several groups^{3,7,10} (4:5:4 pattern at δ 3.5, 4.5, and 5.4 for the COT protons on the metal-bonded carbons, the Cp protons, and the COT protons on the nonmetal-bonded carbons, respectively). Furthermore, careful inspection of the spectrum (Figure 2) reveals that the singlets¹¹ at δ 5.1 and 4.7 may be ascribed to species **A**, with integrated intensities of 1.6–1 (8 COT protons:5 Cp protons) allowing identification of the δ 5.1 ppm resonance as being due to the cyclooctatetraene protons. Excluding the unlikely possibility that species **A** contains a planar COT ring, we must conclude that it is a fluxional compound. Based on the known fluxional compounds (COT)M(CO)₃ (M = Fe, Ru, Os),^{13,14} we assign a structure to this species in which the COT ring is bonded as a 1,3 diene to the cobalt (**3**). Although a reversible isomerization of a 1,3- and 1,5-bonded metal diene seems to be without precedent, we note that Smith and Maitlis have recently isolated thermally unstable 1,3-bonded COT complexes (COT)M(η^5 -C₅Me₅) (M = Rh, Ir) which rearrange irreversibly to the 1,5-bonded isomers at 20 °C. Significantly, the 1,3-COT resonances are singlets.¹⁵

At higher temperatures *each* resonance in the (COT)CoCp spectrum broadens, showing that the temperature dependence to the spectrum observed previously^{10,12} is due to the kinetics of the isomerization process, rather than to fluxionality of the 1,5-bonded compound. Quantitative aspects of the NMR temperature dependence are being studied.¹⁶

Bulk electrochemical reduction at -2.2 V produced a solution containing only the 1,3-bonded anion (3⁻). A frozen solution of the anion displayed an intense electron spin resonance spectrum with cobalt hyperfine splittings. The original mixture of **2** and **3** was regenerated by electrolytic reoxidation of the solution.

All of these data are consistent with the following chemistry of (COT) CoCp:



Clearly, the 1,5 isomer is the more stable of the neutral compounds, but the 1,3 isomer is favored in the anion. The shift in stability may be due to the ability of the 1,3 isomer to delocalize the extra electron of the anion among the four metal-bound olefinic carbons. It is apparent from these results that the nature of a metal-polyolefin bond may be sensitive to the formal oxidation state of the metal, and that electrochemical methods may prove useful in designing ways to reversibly alter the nature of the metal-olefin bond.

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- Samples of **3** prepared by refluxing CpCo(CO)₂ and COT under nitrogen with UV irradiation³ were carefully purified by several fractional sublimations to free the sample entirely of the dimer (CpCo)₂COT.
- The starting compound is air stable and simple nitrogen-blanketing techniques were sufficient for most voltammetric experiments. Some bulk

electrolyses have been carried out in a glove box under nitrogen. Supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. Solvents were prepared and equipment was employed as described previously: W. L. Bowden, J. D. L. Holloway, and W. E. Geiger, Jr., *Inorg. Chem.*, **17**, 256 (1978). Potentials are referred to the aqueous saturated calomel electrode.

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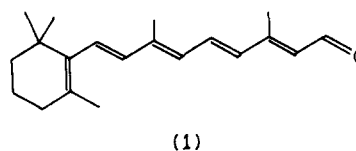
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Fluorescence Lifetime of *all-trans*-Retinal at 77 K¹

Sir:

all-trans-Retinal (**1**) shows spectroscopic anomalies such as diffuseness of the absorption spectrum at 14–300 K,² excitation wavelength (λ_{ex}) dependence of ϕ_{F} ,^{3–9} temperature dependence of radiative lifetime,⁵ τ_{F}^0 , calculated from the relation $\tau_{\text{F}}/\phi_{\text{F}} = \tau_{\text{F}}^0$, an unusually large "Stokes" shift,^{2–7} and a large disparity between τ_{F}^0 from the integrated absorption band (Bu \leftarrow Ag) and τ_{F}^0 from the measured quantity, $\tau_{\text{F}}/\phi_{\text{F}}$.^{2–5,7}



Of these anomalies, the λ_{ex} dependence of ϕ_{F} is most intriguing. Recently, it has been shown that the λ_{ex} dependence can be largely accounted for in terms of a hydrogen-bonded *all-trans*-retinal as the emitting species.⁴ Thus, an intrinsic fluorescence quantum yield of *all-trans*-retinal has been shown to be independent of λ_{ex} within 25%.^{4b} An equilibrium involving a dimeric *all-trans*-retinal (fluorescent) has also been suggested as an additional contributor to the wavelength dependence.^{4c,6}

Since the λ_{ex} dependence of ϕ_{F} has not been examined in terms of fluorescence lifetime which can be used to discriminate contributions of the ground-state and excited-state properties of retinal to the wavelength-dependent fluorescence, we have measured τ_{F} of *all-trans*-retinal in ethanol as a function of λ_{ex} . We have chosen ethanol as the solvent for the following reason: the λ_{ex} dependence of ϕ_{F} persists in ethanol, even though (a) nearly all of the retinal should be hydrogen bonded to the solvent molecules during freezing to and at 77 K^{5,6} and (b) a rapid proton tunneling within the retinal-ethanol H-bonding pair, RC=O...HOEt, may occur along the H-bonding potential curve in the excited state. If the latter occurs prior to fluorescence emission, the expected λ_{ex} dependence of ϕ_{F} due to the H-bonding of retinal can be minimized because of the inequality between equilibrium constants, K and K^* , in the ground and excited states, respectively:

$$K = \frac{(\text{RC}=\text{O})(\text{EtOH})}{(\text{RC}=\text{O}\cdots\text{HOEt})} > K^* = \frac{(\text{RC}=\text{O}^*)(\text{EtOH})}{(\text{RC}=\text{O}^*\cdots\text{HOEt})}$$

The above inequality is predicted from the increase in π -elec-

Table I. The Fluorescence Lifetime and Quantum Yields of *all-trans*-Retinal as a Function of Excitation Wavelength

λ_{ex} , nm	$\tau_F \pm 0.1$ ns	$\phi_F \pm 0.002$
440	0.61	0.064
420	0.73	0.033
400	0.75	0.025
380	0.69	0.017
360	0.67	0.012
340	0.76	0.015

tron density of the carbonyl oxygen of *all-trans*-retinal from 1.399 in the ground state to 1.414 in the excited state.

Immediately prior to the measurements of fluorescence intensity and lifetime data, *all-trans*-retinal (Sigma Chemical Co.) was purified on silica gel TLC in *n*-hexane-ethyl acetate (30:5, v/v) and then extracted into freshly distilled spectro-quality ethanol (U.S. Industries). All procedures were carried out in near darkness.

The fluorescence lifetime measurements were made on an SLM Model 480 phase-modulation fluorometer previously described⁸ and fitted with a holder for liquid nitrogen optical Dewar and cell. All measurements were made with a 1-kW Xe arc lamp as a light source at 1-nm excitation band pass. Corrected emission spectra were measured on a Perkin-Elmer MPF3 spectrofluorometer at 77 K. The excitation bandpass was kept constant at 2 nm throughout the measurement. The relative quantum yield of fluorescence was calculated from the relationship

$$\phi_F = \phi_F^r \left(\frac{\int I_F^s(\tilde{\nu}) d\tilde{\nu}}{\int I_F^r(\tilde{\nu}) d\tilde{\nu}} \right) (A_\lambda^r/A_\lambda^s) (n_r^2/n_s^2)$$

where ϕ_F^r is the quantum yield of the reference compound, riboflavin tetrabutylate⁹ or 9,10-diphenylanthracene,¹⁰ n_r and n_s are refractive indexes of reference and sample solutions at 77 K, respectively, and I_F and A_λ are fluorescence intensity and absorbance, respectively. The absorbances for reference and sample at each wavelength were kept within 5% in order to minimize errors due to the series approximation to the $(A_\lambda^r/A_\lambda^s)$ term in the above equation and the difference in spectral shape of the excitation spectra of reference and samples at a given wavelength band pass (2 nm). In addition, the absorbances at each λ_{ex} were kept within $\pm 12\%$ in order to minimize errors due to light scattering.

Table I presents the measured fluorescence lifetimes and quantum yields as a function of exciting wavelength. Each lifetime is an average of at least 20 phase shifts and modulation measurements. It can be seen that the lifetimes remain essentially constant across the excitation band covering the absorption maximum and the long wavelength edge region, while the fluorescence quantum yields are wavelength dependent in the same spectral region.

The results in Table I strongly suggest that the fluorescence of *all-trans*-retinal in ethanol at 77 K is largely due to one emitting species, as the phase shift and modulation lifetimes were identical within 200 ps, indicative of a single component decay. Nonetheless, the fluorescence quantum yield depends upon λ_{ex} (Table I and ref 5 and 6) for *all-trans*-retinal in ethanol at 77 K. This suggests that a rapid interconversion between free and H-bonded retinal does not occur during the excited-state lifetime (cf. reason b above).

It is also noteworthy that the fluorescence quantum yield of retinal still shows λ_{ex} dependence in the presence of a saturating concentration of KI (85 mM) which enhances fluorescence as a result of R—C=O...K⁺ complex formation.⁵ The lifetime also increases with KI by a factor of 2.¹¹

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Quinuclidin-4-yl

Sir:

Long-range orbital interactions in saturated systems can occur either by "through-space" or "through-bond" mechanisms.¹⁻⁴ The bridgehead positions in a bicyclooctane structure⁵ provide a particularly attractive framework for studies of such interactions. The lone pairs on the two nitrogen atoms of diazabicyclooctane (**1**) provide a four-electron case. Both experimental⁶⁻⁸ and theoretical^{1,3,4} evidence suggest that there is a very strong (~ 1.6 eV) interaction between these two orbitals. Calculations^{1,3,4} indicate that direct overlap is small and that the interaction occurs by a "through-bond" coupling of the nitrogens' lone-pair orbitals with the low-lying σ C-C bond orbitals. One-electron systems include bicyclooctyl⁹ (**2**) and the quinuclidine radical cation¹⁰ (**3**). The magnitudes of $a^{\text{H}\delta}$ in the EPR spectra of **2**⁹ and **3**¹⁰ imply that, while there is some "through-bond" coupling to the 4 position, it is not particularly strong.¹¹ That is, in **2** and **3** the unpaired spin is localized at the formal radical center. Therefore, these radicals are not stabilized¹² and, because they are bridgehead radicals, may even be slightly destabilized. The most important three-electron cases previously studied are **4**, the radical cation of **1**,^{6,13-15} and the radical cations derived from structurally related bicyclic diamines¹⁶ and cyclic disulfides.^{17,18}

The EPR spectrum of **4** shows two equivalent nitrogens and twelve equivalent hydrogens.^{6,13} This was initially interpreted as a fast electron transfer between the nitrogens,⁶ which implies a fairly weak interaction between localized orbitals and, presumably, a radical which is, at most, only slightly stabilized. However, it seems much more likely that **4** is very strongly stabilized.^{4,7,8,13-15} Hoffmann et al.⁴ first suggested "the electron is in fact delocalized over the molecule" and this view is supported by the results of a PES study of **1**,^{7,8} by a more

