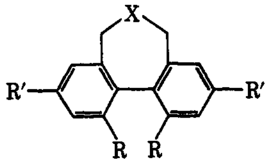
Phosphorescence of Bridged Biphenyls in Fluid Solution

Sir:

In the course of a detailed study of the luminescence behavior of a series of bridged biphenyls we have found that several of these compounds (I–IV) exhibit *an anomalous second emission band at room temperature in fluid solution.* Long-lived emission is typically found only in rigid matrices or at relatively low temperatures since the long-lived triplet state is sensitive to collisional quenching.[1–4] There are only a very few well-documented cases of room temperature phosphorescence in fluid medium.[1,5–7]



I, $X = NCH_3$; $R = R' = H$
II, $X = NCH_3$; $R = R' = CH_3$
III, $X = C{=}O$; $R = R' = H$
IV, $X = C{=}O$; $R = CH_3$; $R' = H$

Compounds I–III were prepared by standard literature procedures. Compound IV was kindly donated by Professor K. Mislow. Biphenyl was a zone-refined sample obtained from Aldrich Chemical Co. Purity was carefully monitored by glpc. Spectral data for the azepine (I), tetramethylazepine (II), ketone (III), dimethyl ketone (IV), and biphenyl are collected in Table I.

Table I. Luminescence Data for Bridged Biphenyls I–IV

Compd	T, °K	$\lambda_{max}^{Absorption\,a}$	$\lambda_{max}^{fluorescence\,a}$	$\lambda_{max}^{phosphorescence\,a}$ Alcohol[b]	$\lambda_{max}^{phosphorescence\,a}$ Alkane[b]	τ_p
I	RT[d]	242	320	456	394	<1 μsec[c]
	77		321	460	468	2.70 sec
II	RT	242	320	410	366	
	77		320	440	442	4.04 sec
III	RT	250	320	404	404	<1 μsec[c]
	77		320	454	464	2.40 sec
IV	RT	246	320	396	398	
	77		320	436	439	3.11 sec
Biphenyl	RT	248	320	Absent		
	77		320	446 471 500		4.5 sec

[a] All peak positions are given in nanometers (nm). [b] Solvent. [c] A Xenon Corp. Novatron 789A nanopulse flash lamp with ~50-nanosec pulse width was used for excitation. [d] RT = room temperature.

All four bridged biphenyls exhibit two emission bands at 77°K (Table I). The emission maxima for these bands are very similar to those of biphenyl. Therefore, it is reasonable to assign the higher energy band as a $\pi-\pi^*$ fluorescence and the lower energy band as a $\pi-\pi^*$ phosphorescence by analogy with the secure assignments made for biphenyl.[8–12] The assignment of the lower energy band is further strengthened by the similar magnitude of the lifetime of this emission and that of biphenyl.

Quite unexpectedly, the solutions of compounds I–IV used for the 77°K measurements when warmed to room temperature still exhibit two emission bands. Only the fluorescence remains in the room temperature spectra of biphenyl. The similarity of the band shape and band maxima of the low-energy room temperature emission to the 77° phosphorescence suggests assignment as a room temperature phosphorescence. Several other possible explanations of the low-energy emission must be considered.

Excimer emission could possibly explain a long wavelength room temperature emission. However, the spectral appearance is unchanged as concentration is varied over two orders of magnitude. Adventitious impurity emission is unlikely since no impurities were detectable by glpc. Furthermore, all four compounds were synthesized from different starting materials, at different times in three different laboratories. Photogenerated impurities are unlikely as the primary source of the emissions since the luminescence spectra are independent of time of illumination. The lifetimes measured for this emission (<1 μsec) while shorter than those measured at 77°K are consistent with those measured for room temperature phosphorescence.[7] The energy of this emission is too low for assignment as $n-\pi^*$ emission in these systems.

Since we have been successful in detecting triplet state esr signals for a series of similar compounds at 77°K,[13] compounds I and III were investigated with irradiation from a 500-W high-pressure mercury lamp in an X-band cavity at room temperature. The samples produced similar two band spectra not found for biphenyl solutions or pure solvent when examined under identical conditions. The more intense high-field line ($g = 2.003$) increases with irradiation time and decays over a period of 1 min after extinction of the light. The weaker, low-field resonance ($g = 2.020$) remains at constant intensity as long as irradiation is continued

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and disappears when the light is extinguished. These esr data are consistent with our assignment of the long wavelength room temperature emission as phosphorescence. The larger g value (2.02) and the bandwidth observed ($\sim$25 G) are characteristic of a delocalized triplet π system. The other signal ($g = 2.003$) is likely due to a solvent radical formed in a solute photosensitized reaction. Such photosensitization generally requires the intermediacy of a triplet species.[14,15]

The rationale for the unique behavior of these biphenyl derivatives is not yet clear but may be due to a mixing of π–π^* and n–π^* states. Such a model has been used to explain the enhanced carbonyl absorption and Cotton effect behavior of IV.[16] The derivatives which do not display this emission (X = single bond, O, S, SO_2) are systems not expected to be capable of such mixing. A full discussion of our findings is deferred to the full paper.

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R. B. Bonner, M. K. DeArmond,* G. H. Wahl, Jr.*
Department of Chemistry, North Carolina State University
Raleigh, North Carolina 27607
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Solvent Effects and the Circular Dichroism Spectra of Metal Complexes

Sir:

The circular dichroism spectra observed in the regions of the d–d transitions of metal complexes which are dissymmetric only because of their conformational structure or because of vicinal effect dissymmetry are currently the subject of intensive investigation. These studies tacitly assume that the solution circular dichroism spectra of these complexes are largely representative of the spectra which would be observed if these molecules were free of their solvent environment. In the course of our fairly extensive studies of the circular dichroism spectra of polyamine systems, we have found that this assumption is rarely correct. We wish to draw attention to this problem here where we describe perhaps the most spectacular example of solvent variation we have observed.

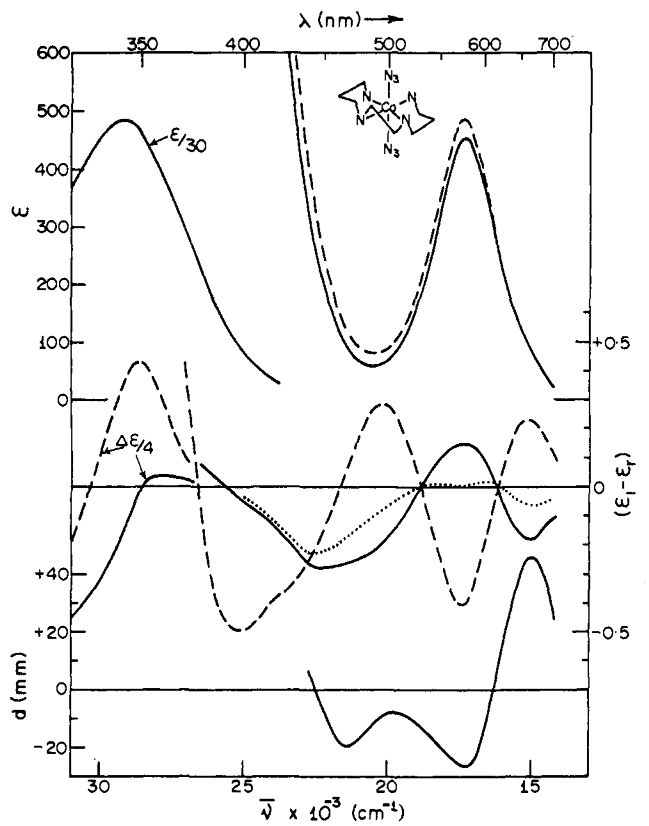

Figure 1. The absorption and circular dichroism spectra of the *trans*-(*R*,*R*)-[Co-3,2,3-tet(N_3)$_2$]ClO_4 complex in water (——), DMSO (- - - -), and 50% water–DMSO (· · · ·). The KBr disk spectrum (——) is shown at the bottom.

The complex ion *trans*-(*R*,*R*)-[Co-3,2,3-tet(N_3)$_2$]$^+$ (3,2,3-tet = $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$) has been resolved and its absolute configuration has been unambiguously correlated[1] with the *trans*-(*R*,*R*)-[Co-3,2,3-tet-Cl_2]NO_3 complex, the absolute structure of which has been determined by X-ray analysis.[2] Figure 1 shows the absorption spectrum of the azido complex in water and dimethyl sulfoxide (DMSO) and the circular dichroism spectra in water, DMSO, and a 1:1 volume solution in water and DMSO. The first two circular dichroism bands at around 15,000 and 17,500 cm^{-1} represent the components of the $^1A_{1g} \rightarrow {}^1E_g$ transition and the (overlapped) band at 20,500 cm^{-1} is the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition. All three of these components are derived from the $^1A_{1g} \rightarrow {}^1T_{1g}$ cubic transition which is split by the largely D_{4h} field. It will be evident that the circular dichroism spectra in water and DMSO are practically enantiomorphous for these three components, and it is only in the higher energy regions, due mainly to charge-transfer transitions, that the circular dichroism in the two solvents becomes approximately similar. A tenfold dilution of the solution or the addition of a 1000-fold excess of ClO_4^- ions over the complex ion concentration does not alter the spectrum in DMSO; a 1000-fold excess of Cl^- ions over the complex concentration does lead to a small change in intensity but there is not a change in sign of any of the components. This last observation suggests that ion multiplets do not cause the effects we are observing. This seems to leave either of two possible explanations: (1) that these effects are due to conformational changes or (2) that the conformations do not change from solvent to solvent but that the effects are in some way caused by the solvent.

Taking the former postulate first, we note that the two terminal six-membered rings are flexible and that it is conceivable that a conformational equilibrium exists where the terminal rings are flipping from the nonchiral chair to the chiral–skew conformations (Figure 2). It will be evident that, because of the chiral constraints imposed by the inner secondary nitrogen atoms, the outer rings in the skew conformation will have the opposite twist sense to the inner

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