

Heavy-Cation-Induced Phosphorescence of Alkanones and Azoalkanes in Zeolites As Hosts: Induced S_1 ($n\pi^*$) to T_1 ($n\pi^*$) Intersystem Crossing and S_0 to T_1 ($n\pi^*$) Absorption

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Previously, we reported that faujasite and pentasil zeolites, exchanged with heavy cations (e.g., Rb^+ , Cs^+ , Tl^+), represent important new and general media for observation of heavy-atom effect^{1,2} and that the magnitude of the effect is large.³ All examples (aromatics and polyenes) provided thus far, involve intersystem crossing from S_1 to T_1 both of $\pi\pi^*$ character. The rules for intersystem crossing (ISC), proposed by El Sayed, indirectly imply that the heavy-atom effect should be observable even in systems where ISC occurs between the singlet and triplet states of $n\pi^*$ character.⁴ There are no examples which illustrate the feasibility of the heavy-atom effect during ISC between states of $n\pi^*$ character. Such examples are provided now in this report.

The two systems we have examined in this context are alkanones and azoalkanes, both of which are suggested to undergo ISC from the excited singlet to excited triplet states, both of $n\pi^*$ character.⁵ Both have lowest $n\pi^*$ S_1 and T_1 states, and no triplet states (such as T_2 $\pi\pi^*$) exist between the S_1 and T_1 states. The energy of separation between S_1 and T_1 is much smaller in alkanones (<5 kcal/mol) than in azoalkanes (~ 15 kcal/mol).

The emission spectra of adamantanone at 77 K included within NaY and TIY are provided in Figure 1. The emission maxima in NaY and TIY are at 405 and 435 nm. The excitation spectra (not shown) for the two emissions are identical to the absorption spectrum of adamantanone. Based on the fact that the λ_{max} of fluorescence and phosphorescence of *n*-alkanones and adamantanone are at 408 ± 4 and 430 ± 10 nm,⁶ we assign the emissions from adamantanone in NaY and TIY to fluorescence and phosphorescence. The emission spectra recorded at 77 K under identical experimental conditions for the same loading level of 5-undecanone included within NaY and TIY are provided in

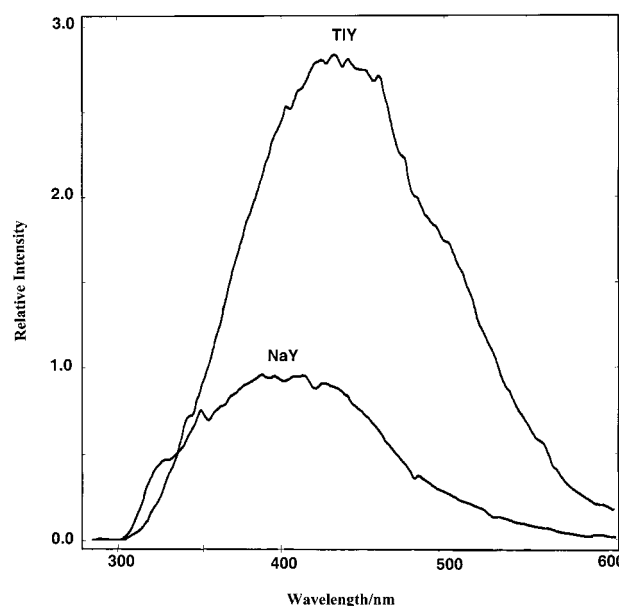


Figure 1. Emission spectra, recorded at 77 K, of adamantanone included in NaY and TIY. Excitation wavelength was kept at 280 nm.

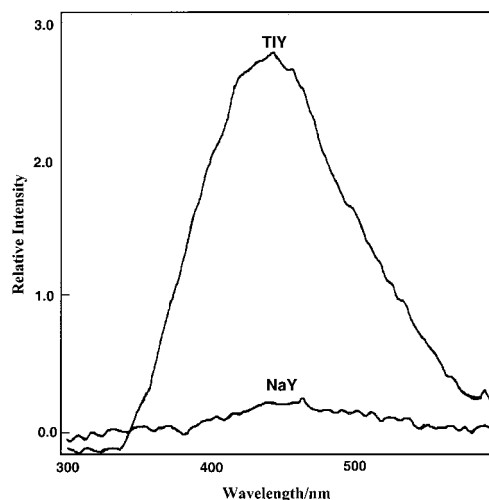


Figure 2. Emission spectra, recorded at 77 K, of 5-undecanone included in NaY and TIY. The excitation wavelength was kept at 280 nm. Spectra were recorded under identical conditions and for the same loading level of the ketone within NaY and TIY.

Figure 2. The emission maxima are near 430 nm in these two samples. On the basis of literature reports,⁶ we attribute the emission to phosphorescence from the ketone. Consistent with the fact that the heavy cation Tl^+ favors ISC, the relative intensity of emission is much higher in TIY than in NaY.

Numerous studies on azoalkanes have established the very poor ISC in them, as well as the lack of phosphorescence even in the presence of a heavy atom perturber.^{7,8} In Figure 3 we show the

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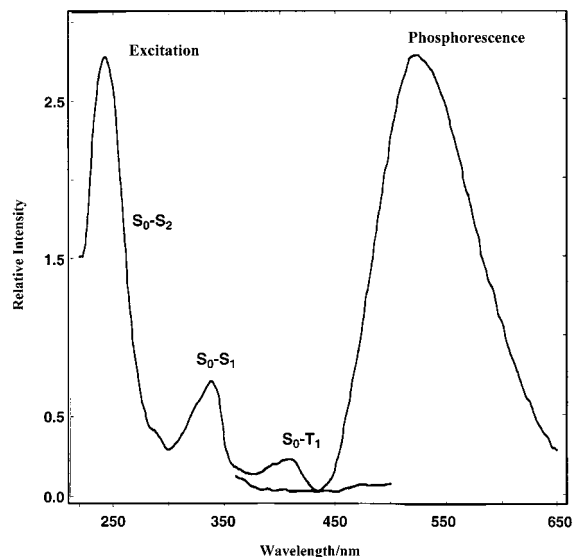
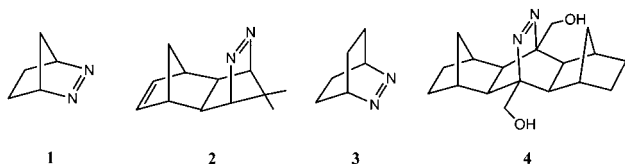


Figure 3. Emission and excitation spectra, recorded at 77 K, of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH; **1**) included in TIY. For the emission spectrum excitation was kept at 340 nm, and for the excitation spectrum the emission was monitored at 508 nm.

Chart 1



phosphorescence emission spectrum at 77 K of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH; **1**) included in TIY. In view of the fact that no phosphorescence has been seen from DBH and its triplet energy has been estimated only by indirect measurements, the observation of direct phosphorescence is remarkable. To verify that the emission from DBH is phosphorescence, we recorded the emission from azoalkane **2** (Chart 1), which is known to phosphoresce (Supporting Information) and monitored the lifetime of the emitting state. The observed phosphorescence emission in TIY at 77 K is identical to the one reported recently for this DBH derivative in EPA glass.^{8b} Notable features in the emission and excitation spectra of azoalkane **2** within TIY zeolite are the following: (a) Unlike in EPA glass, no fluorescence is seen in the TIY samples; (b) the excitation spectrum shows both S_0 to S_1 and S_0 to T_1 transitions; (c) a mirror-image relationship between the S_0 to T_1 absorption and T_1 to S_0 emission is observed. In EPA glass, no S_0 to T_1 absorption was evident in the excitation spectra. The lifetime estimated in the case of azoalkane **1**, by time-resolved emission measurements, was 212 ms (the major component 93%; the minor component 36 ms; see Supporting Information for a decay trace).

The emission maximum at 508 nm seen for DBH (Figure 3) is very close to the emission maximum observed for the DBH derivative **2**. The excitation spectrum shown in Figure 3 consists of S_0 to S_2 , S_0 to S_1 , and S_0 to T_1 absorptions. The excitation spectrum generated by monitoring the phosphorescence emission resembles the absorption spectrum of DBH (see Supporting Information). The triplet-energy estimate (64 kcal/mol) based on the onset (445 nm) of phosphorescence is closer to the photoacoustic calorimetric value.^{7a} The estimated lifetime and triplet energies, similar to the spectrum of the azoalkane **2**, suggest that the observed emission from DBH within TIY is indeed phosphorescence. Consistent with the behavior of DBH, its derivatives (seven in total) within the TIY zeolite showed phosphorescence only (see Supporting Information).

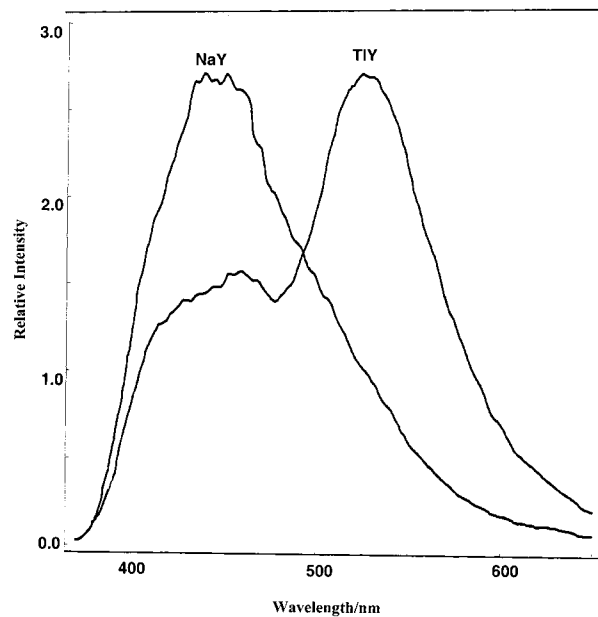


Figure 4. Emission spectra, recorded at 77 K, of azoalkane **4** included in NaY and TIY. The emission spectra were recorded by exciting the sample at 350 nm.

The parent 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO; **3**) did not show phosphorescence when included within TIY; however, several DBO derivatives showed both fluorescence and phosphorescence.⁹ A typical spectrum obtained for azoalkane **4** within NaY and TIY are provided in Figure 4; the spectra for the others are given in the Supporting Information. The excitation spectra, as in the case of DBH derivatives, consisted of S_0 to S_2 , S_0 to S_1 , and S_0 to T_1 transitions. The phosphorescence maxima were at slightly longer wavelength (530 nm) than those of the DBH derivatives, consistent with the estimated lower triplet energy of DBO.^{7a,7b} Prior to this report, no phosphorescence spectra from DBO and derivatives have been published.

The ability to observe phosphorescence from DBH within the TIY zeolite at 77 K is remarkable, considering the unsuccessful attempts that have been made previously to observe phosphorescence from DBH both at 77 K (EPA glass) and in a xenon matrix at 15 K. We have shown in this report that Tl^+ ions present in zeolites induce phosphorescence from systems that involve ISC from S_1 to T_1 , with $n\pi^*$ character. Our earlier observations³ with polyenes and the current results with azoalkanes establish that Tl^+ -exchanged zeolites are powerful matrices to observe phosphorescence from organic molecules that do not phosphoresce under normal conditions.¹⁰

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Supporting Information Available: Experimental details, structures of azoalkanes used in the study, emission spectra of DBH and DBO derivatives (12 azo alkanes in total) and time-resolved emission spectra of DBH, adamantanone, and 5-undecanone in TIY at 77 K (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(10) Experimental procedure provided in the Supporting Information.