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# Complex Formation between Sensitizing Dyes and Stabilizers: A Possible Contributing Factor in Supersensitization*

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We have provided evidence, from fluorimetric titration and analysis of the spectral distribution of fluorescence. that representative symmetrical cyanine dyes, **DTCI** and **DTDCI**, form 1:1 complexes with photographic stabilizers, 2-methylbenzimidazole (**MeBz**), 2-mercaptobenzoxazole (**MBO**), tetraazaindene (**TAI**), and the conjugate anions of the latter two compounds, in solution. AM1 semi-empirical and molecular mechanics calculations are introduced to interpret these results. Complex formation is consistent with the reported role of these stabilizers in supersensitization given the following possibilities: (1) the complexes may be adsorbed to silver halide surfaces in preference to free dye; (2) incorporation of the complex can disrupt a J-aggregate of the dye, with concomitant decrease in recombination probability in the aggregate; and, (3) insofar as computations suggest a partial charge transfer character to the complexes, they may be energy trapping sites on the grain surface, where electron injection into the grain is facilitated.

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## Introduction

It is now generally recognized[1] that many photographic stabilizers and anti-foggants can, in combination with spectral sensitizing dyes, engender an increase in photographic sensitivity with a wide variety of photographic emulsions. These stabilizers, usually mercaptoheterocycles or the well-known 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (**TAI**), are thought to chemisorb to silver halide grains through formation of surface silver complexes,[1,2] and in some cases the crystal structure of the silver(I) complex of the stabilizer has been reported.[3] Several mechanisms have been proposed for the supersensitizing effect of stabilizers:

(1) since the stabilizer complexes silver ion, it may decrease the concentration of interstitial silver ions in the silver halide grain, leading to a reduction in dispersity of latent image and overcoming the intrinsic desensitization accompanying cyanine dye adsorption;[4,5]

(2) the stabilizer may form an "insulating layer" over sensitivity centers into which photoexcited dye is expected to inject electrons;[6] the presence of this insulating layer should inhibit energy-wasting electron-hole recombination; and

(3) intercalation of the stabilizer molecules into the dye J-aggregates can reduce the domain length in the aggregates; this fragmentation of the aggregates can reduce hole mobility, hence recombination probability[7], as well as lead to an increased rate of electron transfer from photoexcited dye to the grain.[8]

Recent work in our laboratories[9,10] has demonstrated that prototypical cyanine sensitizing dyes can form molecular complexes in solution with a variety of organic heterocycles. If stabilizer molecules likewise form complexes with the dyes in solution, several consequences might be envisioned:

(a) the dye complex might be more or less strongly adsorbed to a silver halide grain surface than the free dye; thus the stabilizer could mediate dye adsorption;

(b) incorporation of the dye complex into a dye J-aggregate could lead to fragmentation of the aggregate, as is often discussed in regards to supersensitization[2,7,8]; and

(c) photophysics of the dye complex would most likely be different than observable for the free molecular dye; thus adsorbed complex might have a greater (or lesser) probability of transferring an electron to the silver halide grain on photoexcitation.

The purpose of this study is to extend the methodology of our previous articles[9,10] to the identification and characterization of ground state complexes, in solution, between prototypical cyanine sensitizing dyes and representative stabilizers which are capable of exhibiting supersensitizing effects in silver halide emulsions. Fluorescence spectroscopy is employed for experimental detection of the complexes, insofar as the complexes exhibit different photophysical behavior compared to the free dye. Semi-empirical and molecular mechanics calcula-

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tions are introduced to provide some perspective on the experimental results.

## Experimental

### Materials

The complexing agents, 2-methylbenzimidazole (**MeBz**), 2-mercapto-benzoxazole (**MBO**), and **TAI**, were obtained from Aldrich Chemical Co., and used as received. Melting points agreed with literature values. Our samples of 3,3'-diethyl-2,2'-thiacarbocyanine iodide (**DTCI**, obtained from H. W. Sands Co.), 3,3'-diethyl-2,2'-thiadicarbocyanine iodide (**DTDCI**, obtained from Eastman Kodak Co.), and 3,3'-diethyl-2,2'-thiatricarbocyanine iodide (**DTTCI**, obtained from Pfaltz and Bauer, Inc.) had previously[11] been shown to be of usable purity. Solutions were made up in EM Omnisolv™ spectrophotometric grade methanol.

### Experimental Methods

Experimental procedures for fluorimetric titration of the cyanine dyes with stabilizers, in order to detect complex formation, basically followed those previously reported.[10] In photographic practice it is usual to add stabilizers at alkaline pH, i.e., as their conjugate anions, both for reasons of solubility and, presumably, to facilitate silver ion complexation.[1] Accordingly they were added to 2.5 mL of the dye ($2 \times 10^{-6}$ M) as a series of 100 µL aliquots of 0.01 M solutions of the stabilizers in 0.01 M methanolic NaOH, while fluorescence, excited at the absorption $\lambda_{max}$ for the dye (555 nm for **DTCI**, 655 nm for **DTDCI**, and 755 nm for **DTTCI**), was monitored at $\lambda_{max}$ for emission (570 nm for **DTCI**, 675 nm for **DTDCI** and 790 nm for **DTTCI**).

Under these conditions we expect **MeBz** to be present as a neutral molecule, given that the parent benzimidazole is reported[12] to exhibit a basic $pK_a$ of 13.2. On the other hand, **MBO** and **TAI** should be present exclusively as their conjugate anions under these conditions. We measured a $\mathrm{pK_a}$ of 7.4 for **MBO** (the basic $pK_a$ of the analogous 2-mercaptobenzthiazole is 6.94 [1]), and the reported[13] $\mathrm{pK_a}$ of **TAI** is 6.27. Accordingly, 0.01 M methanolic NaOH was used as the control solution. It had no discernible effect on the efficiency or spectral distribution of fluorescence from **DTCI**, **DTDCI**, or **DTTCI**. All spectrofluorimetric measurements, including recording of emission spectra, were carried out on a Perkin-Elmer MPF44B spectrofluorimeter, thermostatted at $(20.0 \pm 0.1)^{o}$.

### Computational Methods

Computational modeling of structures was carried out in the SPARTAN environment.[14–16] Starting geometries were estimated by Merck Molecular Force Field (MMFF) calculations. Semi-empirical molecular orbital calculations for geometry optimization, charge distribution, and enthalpies of formation were carried out at the AM1 level. Solvation effects were neglected.

Starting geometries for the complexes were obtained by creating dummy molecules in which one of the aromatic nuclei of the cyanine dye was tethered to the stabilizer molecule by two three-carbon chains. The conformation of this molecule was then optimized by MMFF. The tethering chains were then removed, and the conformation of the resulting "complex" then reoptimized by use of MMFF. This geometry was then used as the starting point for the AM1 calculations. This same stratagem has been used by our group to obtain starting geometries for calculations on other bimolecular complexes.[10]

## Results and Discussion

### Experimental Studies

Fluorimetric titrations of **DTCI**, **DTDCI** and **DTTCI** with **MeBz**, **MBO** and **TAI**, under conditions where the latter two reagents were present only as their conjugate anions, were accordingly carried out. Modulation of fluorescence intensity, suggestive of complexation, was observed on addition of all three stabilizers to the carbocyanine and dicarbocyanine dyes, but not for the tricarbocyanine dye. At least in the first case, fluorescence modulation is diagnostic for complex formation, insofar as the fluorescence lifetime[11,17] of **DTCI** is too short (0.14 ± .02) ns to permit dynamic interaction of photoexcited dye with other solutes. The negative results for experiments with **DTTCI** should not, we believe, be taken to mean that this dye does not form complexes with the stabilizers tested. Alternatively we can consider the possibility that complexes, if formed with **DTTCI**, are spectroscopically indistinguishable from the free dye. Complexes of **DTTCI** with other heterocycles have likewise proved elusive.[10]

Consider the case where both free dye and complex are emissive at the probe wavelength, with relative fluorescence quantum efficiencies $\Phi_o$ and $\Phi_c$ respectively. Then the overall observable fluorescence intensity, $I$, is

$$I = I_o f_{dye} + I_c f_{complex} = I_o(1 - f_{complex}) + I_c f_{complex} \qquad (1)$$

where $f_{complex}$ is the fraction of total dye present in the complexed form, $I_o$ is the fluorescence emission intensity observable when all dye is present as free dye, and

$$I_c = I_o(\Phi_c / \Phi_o) \qquad (2)$$

and $f_c = [C]/([C] + [D])$, which is determined in turn by the complex formation equilibrium constant, $K$, and the concentration of stabilizer present, $[Q]$

$$K = [C]/[D][Q] \qquad (3)$$

Combination and rearrangement of Eqs. 1 through 3 leads to the "double reciprocal" equation

$$f([Q]) = \{1/[(\Phi_c/\Phi_o) - 1]\}(1 + 1/K[Q]) \qquad (4)$$

where $f([Q]) = 1/[(I/I_o) - 1]$.

Experimental data obtained with **DTCI** are shown analyzed according to Eq. 4 in Fig. 1. Similar plots for the data obtained with **DTDCI** are shown in Fig. 2. Parameters of the analyses are listed in Table I. Complex formation constants are surprisingly large in all cases. Variation in quantum yields for fluorescence of the complexes, relative to fluorescence quantum yields of free dyes, found in Refs. 11 and 17, appear to reflect subtle patterns of interacting influences. In some cases $\Phi_c/\Phi_o < 1$ suggests that complexation introduces new deactivation pathways, e.g., complex dissociation, while in other cases where $\Phi_c/\Phi_o > 1$, deactivation pathways present in the free dye molecule, e.g., torsional degrees of freedom in the polymethine chain, are apparently inhibited. The latter effects appear to be predominant in the **MeBz** complexes, while the former obtain with the **MBO** anion.

Additional evidence for complex formation comes from the analysis of the spectral distribution of fluorescence. Difference spectra were obtained by subtracting from the emission amplitudes of the control spectra of

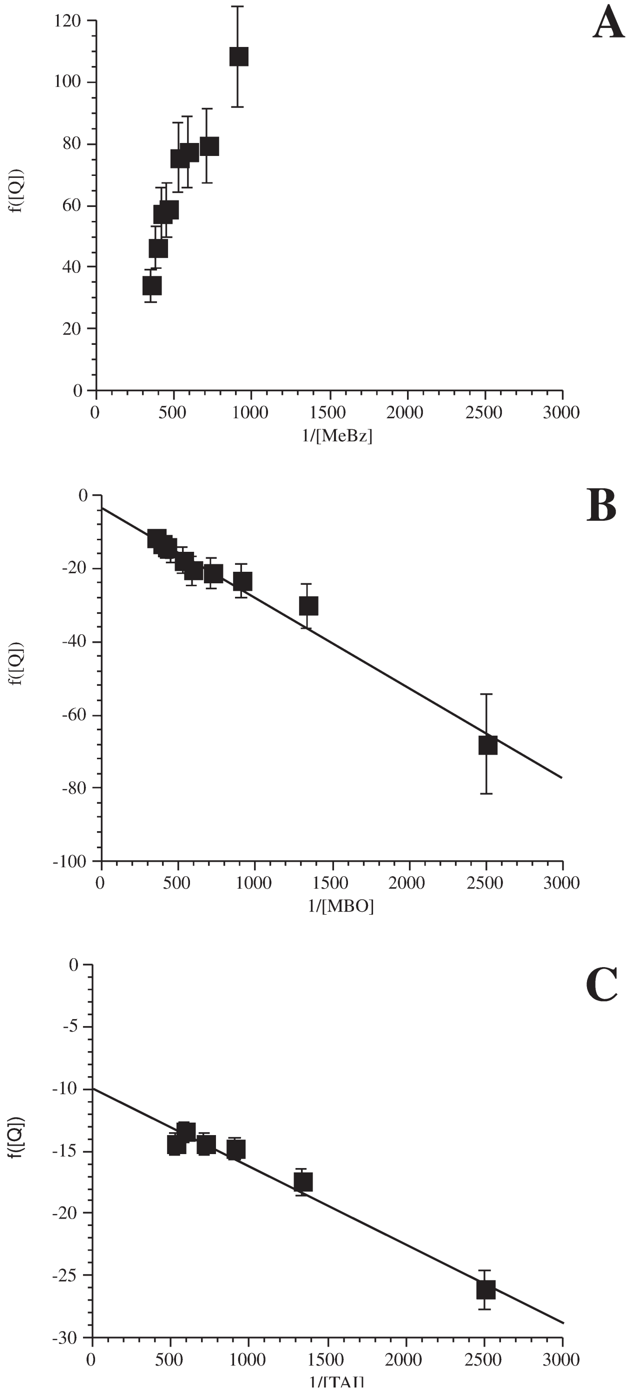

**Figure 1.** Double reciprocal plots according to Eq. 5 for the fluorimetric titrations of **DTCI** with (a) **MeBz**, (b) **MBO** anion, and (c) **TAI** anion.

**TABLE I. Parameters for Dye-Stabilizer Complex Formation from Fluorimetric Titration Experiments (Eq. 4).**

| Dye | Stabilizer | $K$ ($M^{-1}$) | $\Phi_c/\Phi_o$ | $r^2$ | $\Delta G$(kcal/mol) |
|---|---|---|---|---|---|
| **DTCI** | **MeBz** | 35.6 | 1.25 | 0.910 | –2.1 |
| **DTCI** | **MBO** (anion) | 139 | 0.70 | 0.974 | –3.0 |
| **DTCI** | **TAI** (anion) | 1560 | 0.90 | 0.975 | –4.4 |
| **DTDCI** | **MeBz** | 970 | 1.085 | 0.946 | –4.1 |
| **DTDCI** | **MBO** (anion) | 254 | 0.88 | 0.984 | –3.3 |
| **DTDCI** | **TAI** (anion) | 266 | 1.065 | 0.929 | –3.4 |

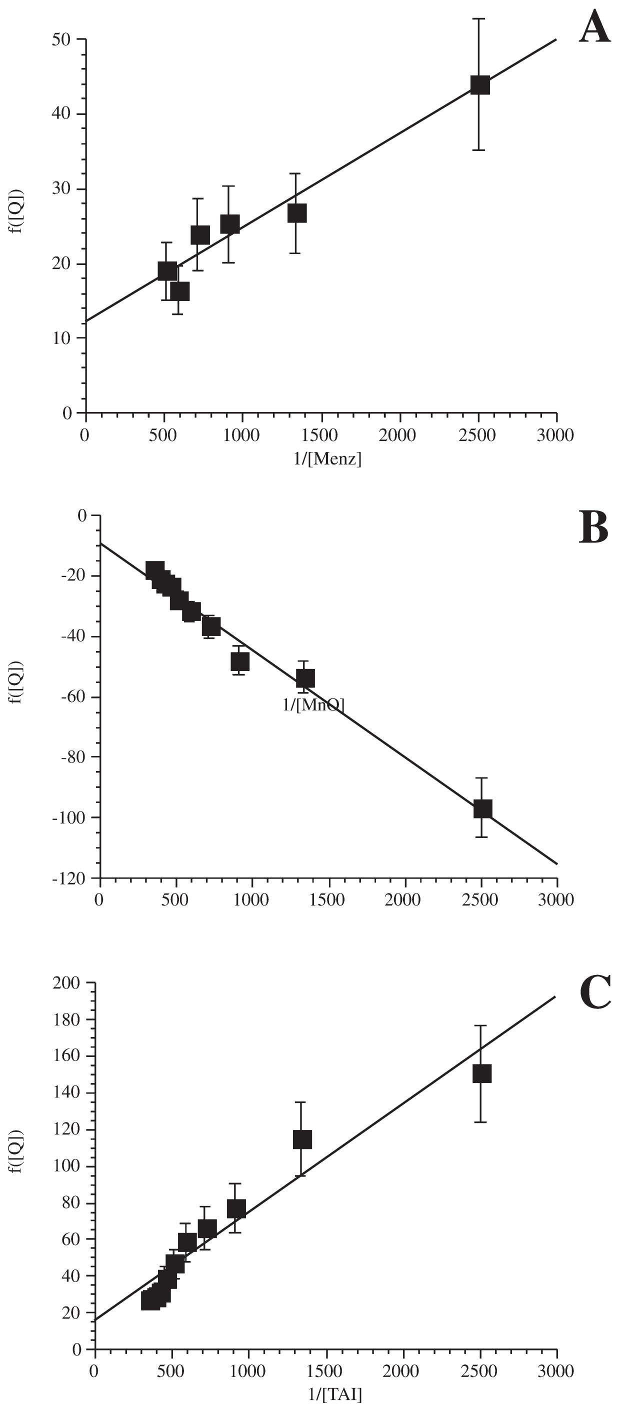

**Figure 2.** As Fig. 1 for **DTDCI**.

**TABLE II. Thermochemical Parameters (kcal/mol) for Formation of DTCI-Stabilizer Complexes from AM1 Calculations (Eq. 5).**

| Stablizer | $\Delta H_f$(dye) | $\Delta H_f$(stabilizer) | $\Delta H_f$(complex) | $\Delta\Delta H_f$ |
|---|---|---|---|---|
| **MeBz** | 305 | 97 | 385 | –17 |
| **MBO** (complex1) | 305 | 91 | 377 | –19 |
| **MBO** (complex2) | 305 | 91 | 362 | –34 |
| **MBO** (complex3) | 305 | 91 | 372 | –24 |
| **MBO** (anion1) | 305 | 14 | 275 | –44 |
| **MBO** (anion2) | 305 | 14 | 260 | –59 |
| **TAI** (complex1) | 305 | 124 | 415 | –14 |
| **TAI** (complex2) | 305 | 124 | 411 | –18 |
| **TAI** (anion) | 305 | 82 | 334 | –53 |

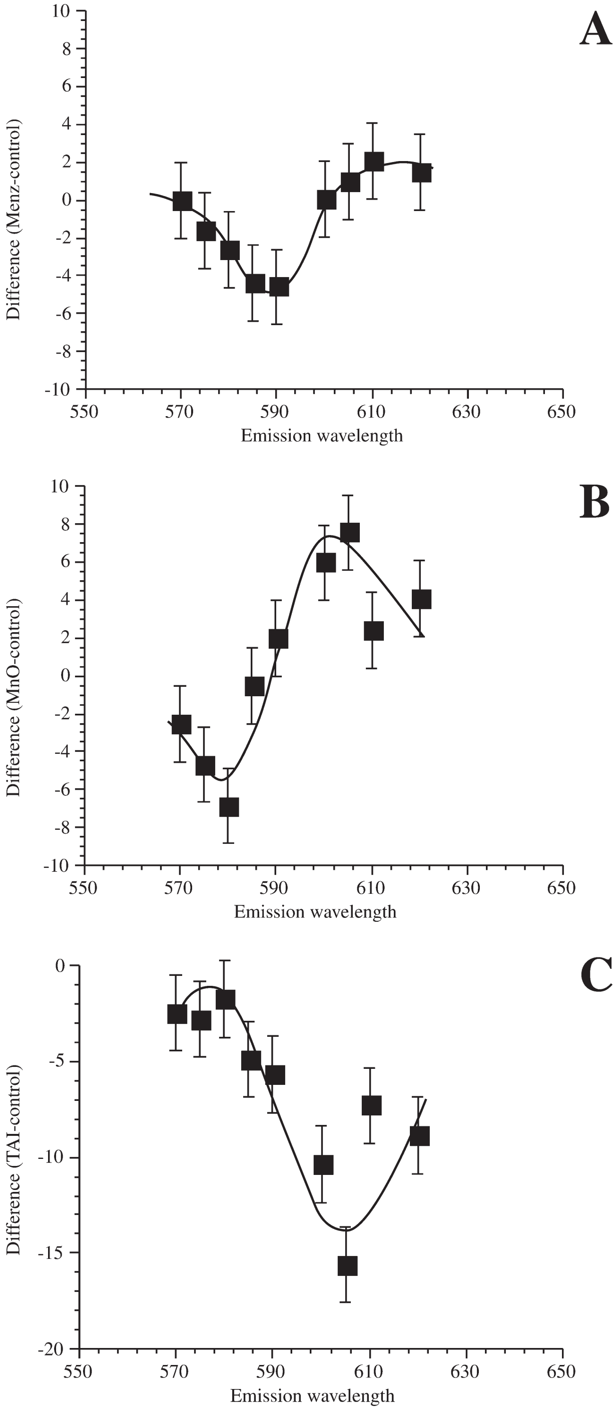

**Figure 3.** Difference fluorescence spectra for **DTCI** with (a) **MeBz**, (b) **MBO** anion, and (c) **TAI** anion, vs. control, showing enhancement (positive difference) or quenching (negative difference) of bands in the vibronic progression to the red of $\lambda_{max}$. Solid curves are only to guide the eye.

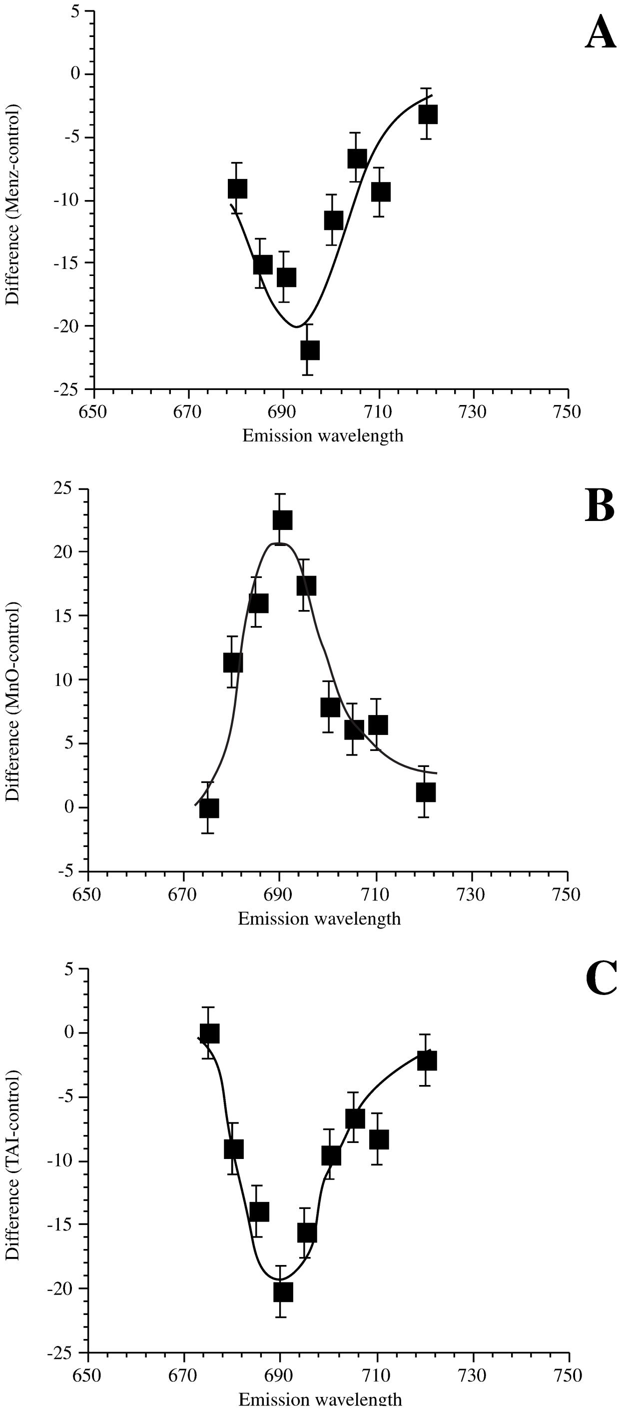

**Figure 4.** As Fig. 3 for **DTDCI**.

the dyes ($2 \times 10^{-6}$ M in methanol) with 0.0028 M NaOH, the corresponding amplitudes obtained from the spectra of the dyes in the presence of 0.0028 M stabilizer and 0.0028 M NaOH, after normalization of the spectra at $\lambda_{max}$ for emission. These spectra for **DTCI** complexes are shown in Fig. 3, and for **DTDCI** in Fig. 4. Changes primarily involve attenuation or enhancement of the long-wavelength vibronic shoulders of the principal emission band. Emission at these wavelengths presumably arises from photoexcited dye molecules at various preliminary stages along the torsional relaxation coordinate leading to radiationless deactivation, according to the model of Momicchioli.[18] Perturbation of emission at these wavelengths is consistent with radiationless deactivation occurring along different relaxation coordinates in the complexes compared to the free dye molecule.

## Computational Studies

Our experimental observations, namely that complexation perturbs the photophysical properties of the cyanine chromophore, suggested involvement of structural deformation and a modicum of charge transfer on complexation. Such effects should be amenable to computational elucidation.

Enthalpies of formation of the complexes from their molecular precursors, $\Delta\Delta H_f$, can be estimated as

$$\Delta\Delta H_f = \Delta H_f(complex) - [\ \Delta H_f(dye) + \Delta H_f(stabilizer)] \quad (5)$$

Insofar as $\Delta H_f$'s derive from AM1 calculations, these estimates may not be more accurate than ± 10 kcal/mol.[13] Recent studies comparing various *ab initio* and semiempirical methods for the description of nucleobase complexes suggests, however, a much higher level of accuracy for AM1 calculations in supramolecular systems.[22] Accordingly, computational estimates of the thermochemical parameters for all the systems studied according to Eq. 5 are reported in Table II to the nearest kcal/mol. These estimates are gas phase enthalpies of formation, which ignore solvation effects, not free energies, are thus not directly comparable to experimentally measurable free energies of complexation, reported in Table I. We note that the experimental parameters are more positive, consistent with the negative entropy of complex formation. Our experience[10,20] has been that the condition, $\Delta\Delta H_f \leq 0$, is a reasonable predictor of strong complexation in several systems.

Both computational and experimental characterization of complexes between **MeBz** and **DTCI** and **DTDCI** has been reported previously.[10] This previous work revealed a complementarity in electrostatic charge distribution between the dye and the heterocyclic complexing agent, so as to provide a strong electrostatic attraction between the two components, when they were positioned relative to each other in the manner found to correspond to the minimum energy conformation of the complex. Accordingly the positively charged S-atom of the dye is centered over the negative charge-bearing heterocyclic ring of the benzimidazole.

The neutral **MBO** molecule exists in the solid state, and, presumably, in solution exclusively in the thione form.[21] At least three conformations corresponding to energy minima ($\Delta\Delta H_f$) within experimental error of each other could be identified in a conformational search for the complexes of neutral **MBO** with **DTCI**. The structure of the energetically most favored of these (complex 2 in Table II) is shown in Fig. 5. Electrostatic charges, indicated on the figure, show that unlike the case of **MeBz** there is no apparent complementarity in charge distribution between the two components of the complex. Two ion pair complexes of the **MBO** anion with **DTCI** were also found. The structure corresponding to the more favorable one is remarkably similar to that of the complex between **DTCI** and the neutral **MBO** molecule, shown in Fig. 5. In the case of the ion pair a strong electrostatic interaction might be expected between the negatively charged S-atom of **MBO** conjugate anion and the positively charged S-atom of the dye, located 3.43 Å away.

Comparison of the electrostatic charge distributions within the cyanine chromophore, and among the complexes, indicates a small but significant introduction of negative charge into the π-electron system of the dye in the latter cases, suggesting a contribution of charge transfer to the driving force for complex formation. To evaluate the possibility of charge transfer interaction quantitatively, the electrostatic charges, $q_i$ on the heavy atoms of the dye molecule were summed, $\Sigma q_i$, for the free dye and for each complex. The degree of charge transfer, $\Delta q = \Sigma q_i(\text{complex}) - \Sigma q_i(\text{free dye})$, could then be estimated as given in Table III. Charge transfer from stabilizer to dye is indicated by $\Delta q < 0$; the opposite condition, $\Delta q > 0$ indicates dye to stabilizer charge transfer. Note that $\Sigma q_i < +1.0$ for the free dye, reflecting delocalization of much of the positive charge in the dye chromophore onto the peripheral hydrogen atoms, presumably by hyperconjugation. The possibility of a charge transfer contribution to complexation may be more important in solution than in the gas phase. In solution, forces developed by electrostatic pattern recognition between the complex partners may be substantially offset by the presence of solvent dipoles.

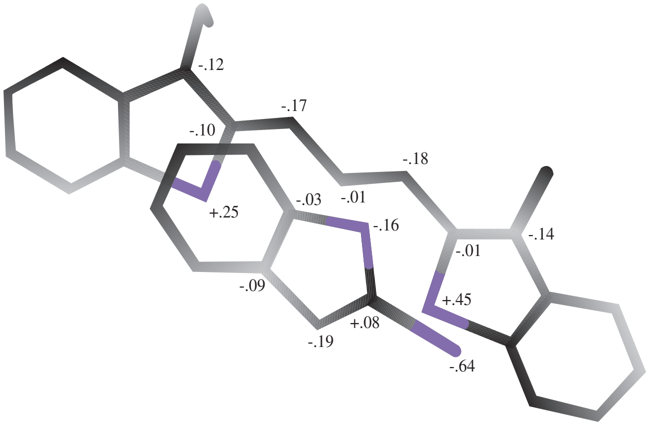

**Figure 5.** AM1 calculated structure for the energetically preferred conformation of the **DTCI**-**MBO** complex.

**TABLE III. Expected Degrees of Charge Transfer (AM1 Calculation) in Complexes of DTCI andd Stabilizers**

| Stabilizer | $\Sigma q_i$ | $\Delta q$ |
|---|---|---|
| free dye | + 0.05 | — |
| **MeBz** | + 0.05 | 0 |
| **MBO** (complex 2) | – 0.03 | – 0.08 |
| **MBO** (anion) | – 0.03 | – 0.08 |
| **TAI** (complex 2) | + 0.01 | – 0.04 |
| **TAI** (anion) | + 0.17 | + 0.12 |

A hypothetical representation of the adsorption of the **DTCI**-**MBO** anion ion pair on the (111) AgBr surface is shown in Fig. 6, based on AM1 and MMFF calculations. (Because SPARTAN 4.0 does not contain a basis set for silver, geometry of the adsorbate on an AgBr grain was projected using a point charge array with spacing corresponding to an unreorganized AgBr (111) crystal plane as a surrogate for the grain surface). No complementarity of charge distributions between the complex and a (100) surface could be discerned. It is thus reasonable that the complex should adsorb preferentially to the (111) surface. Adsorption of the complex appears to be driven primarily by complexation of the stabilizer anion with surface silver ions. The ability of the **MBO**-analog, 2-mercaptobenzimidazole, to form an isolable complex with AgBr has recently been reported.[22] This noteworthy observation provides experimental support for the speculation embodied in Fig. 6. Complexes may thus be adsorbed to AgBr preferentially to free dye.

According to our calculations, neutral **TAI** forms complexes exothermically with **DTCI** only in its amide, or 'oxo', tautomeric form, which, however, is expected[23] to predominate in solution. A representative structure, corresponding to complex 2 of Table II, is shown in Fig. 7. The small decrease in positive electrostatic charge, $\Delta q$,

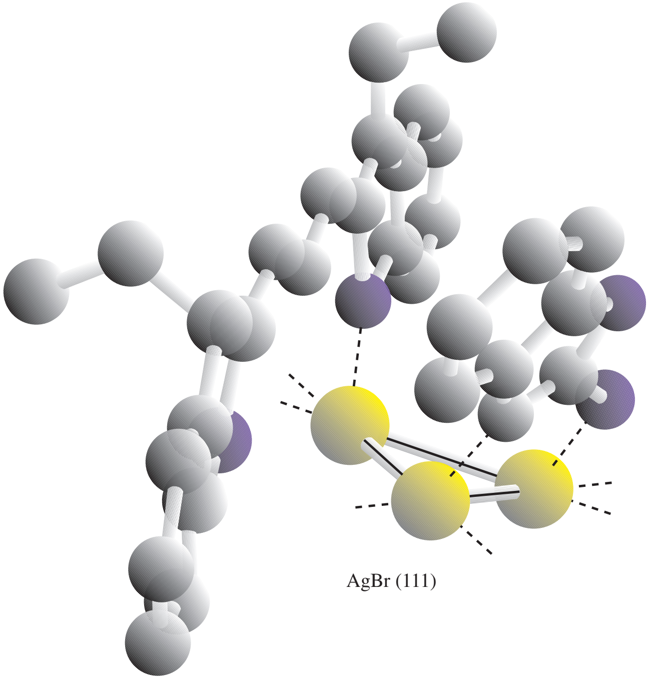

**Figure 6.** Schematic representation of the adsorption of a **DTCI**-(**MBO** anion) ion pair to an AgBr (111) surface based on AM1 and MMFF calculations.

on the atoms of the polymethine chain of the dye in the complexed form again suggests a contribution of charge transfer interaction; see Table III. As was found for the case of **MBO**, complex formation, i.e., ion pairing, is much more strongly exothermic between **DTCI** and the **TAI** anion than with the neutral **TAI** molecule. The energy minimized structure of this ion pair is essentially indistinguishable from that of the complex shown in Fig. 7 Surprisingly, $\Delta q > 0$ in this case, suggesting that charge transfer occurs in this ion pair in the opposite direction to that inferred for the other complexes.

## Conclusions

We have provided evidence that representative symmetrical cyanine dyes, **DTCI** and **DTDCI**, form 1:1 complexes with photographic stabilizers, **MeBz**, **MBO**, **TAI**, and the conjugate anions of the latter two compounds, in solution. Complex formation is consistent with the reported role of these stabilizers in supersensitization considering the following possibilities:

(1) the complexes may be adsorbed to silver halide surfaces preferentially to free dye;
(2) incorporation of the complex can disrupt a J-aggregate of the dye, with concomitant decrease in recombination probability in the aggregate[7]; and
(3) given the indicated charge transfer character of the complexes, they may be energy trapping sites on the grain surface, where electron injection into the grain is facilitated.

In addition, complex formation in solution can provide help to explain order of addition effects seen when sensitizing dyes and stabilizers are added to the same emulsion.[2]

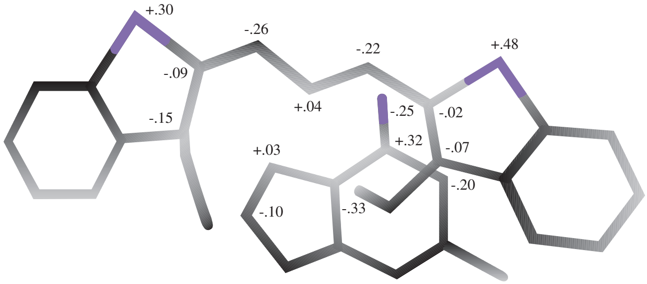

**Figure 7.** AM1 calculated structure for the energetically preferred conformation of the **DTCI-TAI** complex.

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