

Complex Formation Between Thiocyanine Dyes and Aromatic Heterocycles of Photographic Significance

A. F. Marks and M. R. V. Sahyun
Department of Chemistry, University of Wisconsin,
Eau Claire, WI 54702 USA

Introduction

Recently we reported experimental evidence that at least cyanine dyes form ground state complexes with aromatic amines, but not with aliphatic amines of comparable ionization potential.¹ The complexes are experimentally detectable through quenching of the fluorescence of the 3,3'-diethyl-2,2'-thiocyanine cation. This result implies that the aromatic amine mediates excited state relaxation of the cyanine dye. Because the emissive lifetime of this cyanine cation is too short to allow dynamic encounter with potential quenchers in solution, we postulated ground-state complex formation to explain these results. Accordingly, mediation of radiationless deactivation of complexed dye may involve introduction of a new decay pathway, namely non-adiabatic thermalization of excitation energy into complex dissociation.

We felt that these results in the cyanine dye system required further investigation to:

- (i) establish the generality of the phenomenon;
- (ii) confirm its previous interpretation specifically as π -complex formation; and
- (iii) explore its relationship to spectral sensitization in silver halide photography.

For this work we chose a homologous series of symmetrical 3,3'-diethyl-2,2'-thiocarbocyanine dyes, **I**, **II**, and **III**, with 3, 5 and 7 carbon atoms in the polymethine chain, respectively.

The photophysics of these dyes in various solvents have been studied extensively.^{2,3} As model complexing agents we selected imidazole (**Im**), benzimidazole (**Bz**), and 2-methylbenzimidazole (**MeBz**). We also included the photographically active heterocyclic bases, 2-mercaptobenzoxazole (**MBO**) and 2-mercaptobenzimidazole (**MBI**), which are well-known antifoggants,⁴ of the class known to interact with spectral sensitization.⁵ We expected strong π -overlap between the aromatic heterocycles of the cyanine chromophores and the complexing agents. At the same time, we also expected that with these molecules electron-transfer quenching could be excluded. Furthermore, differences in complexing activity between imidazole and benzimidazole should provide a test of our hypothesis that

their interaction with the cyanine dyes represents π -complexation.

Method

The experimental phase of the investigation has been reported.⁶ In the present report we describe the molecular mechanics and quantum chemical analysis of the systems under investigation. Computational chemical studies in the literature on cyanine dyes have largely been directed towards estimation of electronic transition energies, i.e., simulation of absorption spectra, ionization potentials and electron affinities, using relatively primitive computational procedures.⁷ Some MINDO/pm3 calculations have been reported recently.⁸ Molecular mechanics calculations have been used to predict geometries and, accordingly, spectral characteristics of H- and J-aggregates of some cyanine dyes.⁹

Computational modeling of the molecules used in this study was carried out using the SPARTAN package.¹⁰ In general a molecular mechanics geometry search using the Merck molecular force field (MMFF) was carried out to find a minimum energy starting point for appropriate isomers of each compound. The SPARTAN algorithm allowed application of geometric constraints in order to estimate strain energy differences between the minimum energy conformation of a compound and other hypothesized conformations. From this point, a full AM1 (semi-empirical molecular orbital) geometry optimization could be carried out. An Osawa conformation search could then be carried out to re-evaluate the identification of geometries associated with strain energy minima. The AM-1 calculations also yielded electrostatic charge distributions which could be used, see below, to evaluate electrostatic contributions to complex formation.

Operationally complexation is approached in the SPARTAN environment by tethering the dye and complexing agent heterocyclic ring systems together with flexible, typically three-carbon alkane chains for a preliminary geometry minimization. This strategy creates an initial geometry for the complex somewhat in proximity to a potential energy minimum, thereby greatly reducing time required for the molecular mechanics calculations. The chains are then be removed for the actual MMFF and AM1 calculations.

Results and Discussion

Molecular mechanics calculations were carried out on the dyes **I**, **II** and **III**. The minimum energy form of dye **I** was found, using MMFF, to correspond to the *trans*-anti-isomer, in contrast to crystal structure determinations¹¹ which show that crystallization from solution leads exclusively to deposition of the *trans*-syn-isomer. It appears that in the gas phase (and, presumably, in solution) intramolecular dipole-dipole interactions stabilize the anti-conformation, while in the solid state intermolecular dipole-dipole interactions serve to stabilize the syn-conformation.

For dye **II** energy minimization leads again to the anti conformation for the all-*trans* isomer, but only 0.26 kcal/mol below the syn conformation (neglecting any differences in solvation energy between the two isomers). Both structures might be expected to coexist in solution. In this case the two conformations of the all-*trans* isomer exhibit 3.33 and 2.57 kcal/mol less strain energy than their 8,9-*cis* counterpart. Photoisomerization of the all-*trans*-anti isomer is expected¹² to lead to the 8,9-*cis*-syn isomer as the metastable photoproduct.^{13,14} Optoacoustic spectroscopy has indicated an energy difference between the *trans* and *cis*-photoisomers of dye **II** in the ground state as 3.5 kcal/mol in good agreement with the calculations.¹⁴ We accordingly infer an adequate degree of reliability to the MMFF calculations for these dyes, consistent with the general experience in conformational optimization of organic molecular structures.¹⁰ Accordingly MMFF provides a good account in most cases, while semi-empirical molecular orbital methods are, at best, not necessarily reliable. From the MMFF calculations we further infer that in solution, dye **III** is likely to be a mixture of an even greater number of equilibrating isomers, and solvation energy is likely to play a large role in determining which isomer(s) are dominant under given conditions.

With regard to the basis for complex formation, inspection of electrostatic charge distributions in the dye and complexing agent molecules from the AM1 calculations proved especially informative. Surprisingly, in all of the dyes the sum the electrostatic charges associated with the atoms of the π -electron bearing framework was negative, despite the cationic character of the chromophores. This was a reflection of substantial delocalization of positive charge to the peripheral protons of the molecules, presumably involving hyper-conjugation. Hyperconjugation is thought to be involved in the exchange mechanism of *cis-trans* photoisomerization in compounds such as stilbene and

retinal.¹⁵ A similar pathway is a principal route for excitation energy dissipation in cyanine dyes.¹²

The search for minimum energy conformations of dye complexes was initially restricted, for reasons of practicality, to geometries in which the complexing agent, e.g., **Im** or **Bz**, is "sandwiched" with one of the aromatic nuclei of the dye chromophore, i.e., π -complexation. The gas phase enthalpy of formation of the complex from its individual components, ΔE , for any candidate geometry can then be approximated as⁹

$$\Delta E = \sum \sum (\mathbf{r}/4\pi\epsilon)(q_i q_j / r_{ij}^2) - (A_{ij}/r_{ij}^6) + (B_{ij}/r_{ij}^{12}) \quad (1)$$

where q_i and q_j represent the individual electrostatic charges on atoms of the dye and complexing agent, respectively, where r_{ij} is the (scalar) interatomic spacing between each such pair of atoms, and \mathbf{r} is the vector separation between the planes of the dye and complexing agent rings, taken at this point to correspond to the graphitic interlayer spacing, 3.4 Å. Since this value also corresponds to the sum of the van der Waals radii of the carbon atoms in the two ring systems, the second and third terms in eq. 6, corresponding to attractive and repulsive dispersion forces, respectively, cancel out,¹⁶ and only the first term need be evaluated.

Estimates of ΔE for dye-complexing agent combinations according to Eq. 1 are given in Table I. (In the AM1 calculations we also found a small but significant tilt between the planes of the aromatic rings of the dye and complexing agents, ca. 3 - 7°, which was not taken into account in these calculations). Charge distributions for all three dyes in their all-*trans*-syn forms were used. In general, estimates derived from Eq. 1 suggest that **Im** complexes should be stronger than **Bz** complexes, and that dyes tend to form stronger complexes with increasing polymethine chain length. These expectations are not reflected in the pattern of the experimental data,⁶ which are, however, formation constants. The calculated ΔE values are enthalpies, which do not reflect entropic contributions. Accordingly, dyes which initially possess more internal degrees of freedom may exhibit more negative entropy changes on complex formation than simpler, i.e., shorter chain, dyes. Estimates of gas phase binding energies, of course, completely neglect changes in solvation energy on complex formation, which may vary considerably among complexing agents. Gas phase enthalpies of complex formation with the two photographically active complexing agents, **MBI** and **MBO**, were found to be about the same; only the data for **MBI** are reported in Table I.

Table I.-Estimates of gas phase enthalpies of complex formation, $-\Delta E$ (kcal/mol)

Dye	Im	Bz	2-MeBz	MBI
I	9.5	5.8	9.8	28
II	10.9	9.2	20.5	11.5
III	15.7	15.6	24.4	17.5

With these complexing agents, we observed patterns of electrostatic charge distribution, involving the dye-S (positive), a complexing agent heteroatom (negative), and the un-ionized mercapto-S (positive), which were complementary to the charge distribution pattern on the AgBr {100} surface, and which could direct epitaxial adsorption of the dye complexes on that face of the grain. Compounds such as **MBI** and **MBO** are usually thought¹⁷ to chemisorb to AgBr with ionization, forming sparingly soluble salts, with S-Ag bond formation, even though the N-proton in **MBI** is more acidic than the S-proton. AM1 calculations on deprotonated **MBI** and **MBO** showed that the negative charge of the conjugate anion was distributed on the mercapto-S atom and the ring heteroatoms, leading to a charge distribution pattern incompatible with epitaxial deposition of deprotonated complex on the {100} AgBr surface. Simulation of the AgBr {111} surface as a point charge array of appropriate geometry led to a model for chemisorption of deprotonated complexing agent or dye complex. Accordingly the ring-N is monodentate coordinated to one surface silver ion, while the mercapto-S atom is bidentate coordinated to two adjacent surface silver ions. We therefore infer that deprotonated dye complex should selectively adsorb to {111} grain surfaces, while the un-ionized form of the complex should exhibit preferential adsorption on {100} faces.

Conclusions

A combination of molecular mechanics and quantum chemical methods has proven useful to the description of the energetics and structure of complexes formed between a variety of heteroaromatic compounds, including photographically active anti-foggant agents, and cyanine dyes. We find that the primary driving force for complexation is electrostatic, rather than the originally surmised π -interactions. We predict that complexes between dyes and unionized **MBI** or **MBO** may preferentially adsorb epitaxially on AgBr {100} faces, while deprotonation of the heterocycle's mercapto function alters the charge distribution so as to facilitate adsorption on {111} faces.

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