

# A Study on the Hue of the Novel Acylacetanilide Azomethine Dye

Naoki Saito and Seiji Ichijima  
Ashigara Research Laboratories, Fuji Photo Film Co., Ltd.  
Kanagawa, Japan

## Abstract

The X-ray analyses indicate that acylacetanilide azomethine dyes consist of the dye planes with their acyl groups tilted out of the dye planes by about 90°. The electronic effect of the acyl groups on the absorption properties is examined by PPP-MO and MM method. The results show that the longest absorption band ( $\lambda_{\max}$ ) shifts to longer wave-length (a bathochromic shift) with decreased absorption intensity as the dihedral angle between the acyl group and the dye plane goes away from 90°. When the acyl group is indolinylcarbonyl, it is estimated that the bathochromic shift is smaller and that the decrease in absorption intensity is larger compared with other azomethine dyes. This study provides a good explanation for the observed absorption behavior of the acetanilide azomethine dyes.

## Introduction

An acylacetanilide has been used as a yellow coupler in the conventional photographic system. In the developing process a yellow coupler reacts with the oxidized developer to form a yellow azomethine dye. One of the most important properties of the dye is, of course, its hue. It is closely concerned with color reproducibility and optical sharpness. Since the visible region lies above 400 nm, the longer wavelength side of the absorption curve is important for a yellow dye. As for color reproducibility, it is desirable that a yellow dye has a sharp-cut spectrophotometric curve, with decreased absorption in the green region of the spectrum.<sup>1</sup> And larger extinction coefficient is preferred in order to improve the optical sharpness. Great efforts have been made to realize these desirable properties.

In the course of the efforts we found a novel indolinylcarbonylacetanilide azomethine dye (the indolinyl type), which gives excellent absorption properties. The yellow dye in the conventional photographic film is a benzoylacetanilide azomethine dye (the phenyl type).

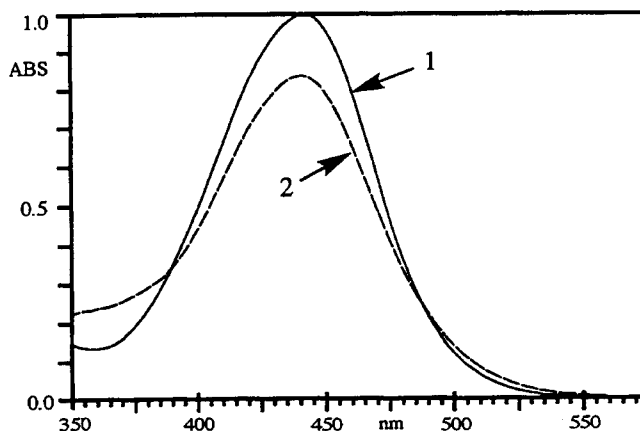
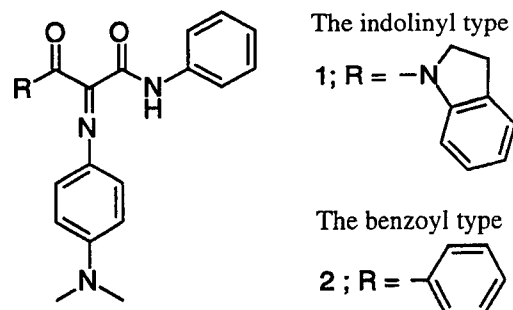
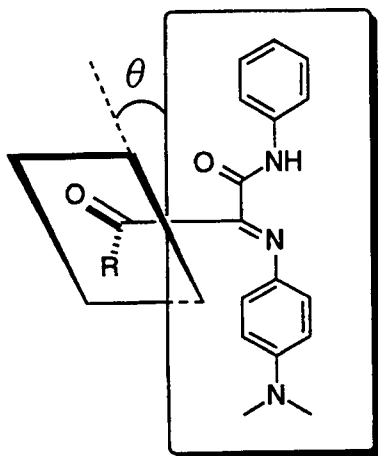


Figure 1. Absorption spectra of the indolinyl type and the benzoyl type in ethyl acetate.

Absorption spectra of these two dyes are shown in Figure 1. As shown in this figure, the indolinyl type has a sharper curve than the phenyl type. Especially in the green region the indolinyl type has much less absorption. The indolinyl type has a larger extinction coefficient than the benzoyl type.

There are very few literature on the hue of azomethine dyes.<sup>2,3</sup> Particularly the relationship between structure of the dye and shape of the spectrophotometric curve has been hardly reviewed. We discuss here why the indolinyl type can give a sharp-cut spectrophotometric curve and a large extinction coefficient. In the first place, the most stable conformation was examined by X-ray analysis. It was cleared that both of the dyes have much the same dye planes and

each acyl group tilted out of the dye plane by about  $90^\circ$  ( $\theta \cong 90^\circ$ ).<sup>4</sup> Therefore in both cases the longest wavelength absorption band is attributed to the excitation from the highest occupied MO (HOMO) to the lowest unoccupied MO (LUMO) in the dye plane common to these dyes.



### Calculation and Discussion

The PPP-MO method is known to be very reliable for the calculation of  $\pi$  electron exciting energies,<sup>5</sup> but this method is basically used for planar geometry. In order to take account of the C-C bond torsion, ' $\beta \cos\theta$ ' is used as the resonance integral ( $\beta$ : the resonance integral when the acyl group and the dye plane are coplanar). Figure 2 shows plots of the longest wavelength absorption band ( $\lambda_{\max}$ ) against dihedral angle ( $\theta$ ). These results indicate that in both cases bathochromic shifts are observed when tilt of acyl group is far from  $90^\circ$ , and that the bathochromic shift is much larger especially in the region under  $90^\circ$  when R is phenyl. This difference in the absorption behavior is considered to be one of the reasons why the indolinyl type could give a sharp-cut absorption curve than the phenyl type.

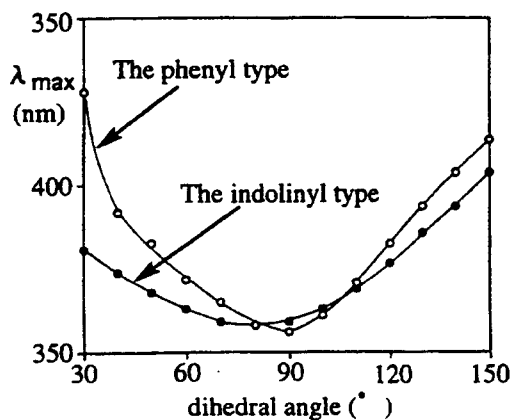


Figure 2. Plots of the longest wavelength absorption band ( $\lambda_{\max}$ ) against dihedral angle ( $\theta$ ).

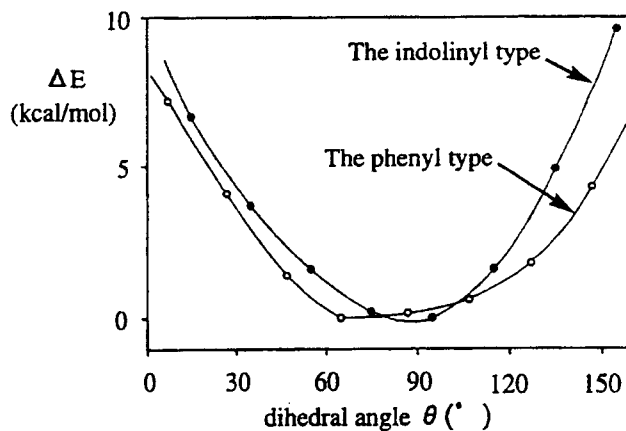


Figure 3. Plots of heat of formation ( $\Delta E$ ) against dihedral angle ( $\theta$ ).

The energy differences between each conformation and the most stable one are estimated by the MM3 method.<sup>6</sup> The results are summarized in Figure 3. The optimizations of the dihedral angles of both dyes produce values of about  $90^\circ$ . These conformations agree with the results of X-ray analysis. Figure 3 also indicates that it is much easier for both of acyl groups to tilt toward smaller value of the dihedral angle, furthermore that the phenyl type is able to tilt more easily than the indolinyl type. Then the indolinylcarbonyl group vibrates within much smaller range than the benzoyl group at a given temperature. This result by MM3 method is also considered to be one of the reasons why the indolinyl type gives a sharp-cut absorption curve.

Oscillator strength ( $f$ ) is also estimated by PPP-MO method. Figure 4 shows plots of oscillator strength ( $f$ ) against dihedral angle ( $\theta$ ) and the longest wavelength absorption band ( $\lambda_{\max}$ ). This figure indicates that the more bathochromically the absorption bands shift, the smaller the oscillator strength would be, and that the oscillator strength of the indolinyl type decreases more immediately than that of the phenyl type. Moreover Figure 4 shows that the oscillator strength of the indolinyl type is larger than that of the phenyl type when dihedral angle is above  $40^\circ$ , and on the contrary, that the oscillator strength of the phenyl type is larger when dihedral angle is under  $40^\circ$ . These results successfully explain why the indolinyl type gives a sharper absorption curve and a larger extinction coefficient than the phenyl type.

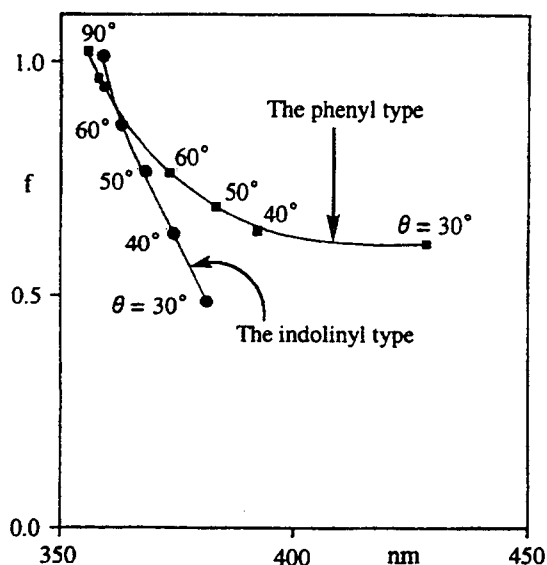
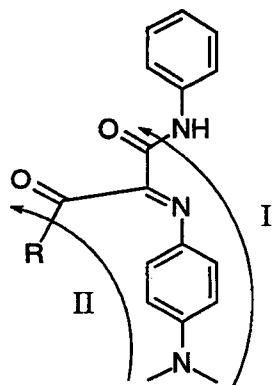


Figure 4. Plots of oscillator strength ( $f$ ) against the longest wavelength absorption band ( $\lambda_{max}$ ) and dihedral angle ( $\theta$ ).

It is discussed why the indoliny type has a larger oscillator strength than the phenyl type when dihedral angle is close to  $90^\circ$ . The lowest transitions of the two dyes (the indoliny type and phenyl type) are examined by PPP-MO method. It is indicated that the lowest transition mainly consists of the excitation from HOMO to LUMO. HOMOs of the two dyes are much the same, but there are some differences between their LUMOs. LUMO of the indoliny type has larger coefficients at the carbonyl group on the dye plane, but has much smaller coefficients at the twisted acyl group than that of the phenyl type.



Transition moment is considered to consist of two vector components which are the main component I (on the dye plane) and the subcomponent II (to the twisted acyl group out of the dye plane). The indoliny type has the larger main component I and the smaller subcomponent II compared with the phenyl type. In other words, dispersion of vector

components is observed in the case of the phenyl type. Therefore the indoliny type has a larger transition moment. The small subcomponent II in the indoliny type would be attributed to the electron-donative property of the nitrogen atom in the 5-membered heterocyclic ring. This characteristic property could effectively prevent the charge transfer to the twisted acyl group.

## Summary

The large extinction coefficient and the sharp-cutting spectrophotometric curve of the indoliny type are explained by our calculated results as follows. It is hard for the indoliny carbonyl group to tilt far from the most stable conformation ( $\theta \approx 90^\circ$ ). Moreover this novel dye gives a larger oscillator strength when the dihedral angle is close to  $90^\circ$ . Departing from  $90^\circ$ , on the contrary, the oscillator strength decreases immediately with a relatively smaller bathochromic shift.

## References

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