



Comparison of the INDO/S and the CNDO/S Method for the Absorption Wavelength Calculation of Organic Dyes

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ABSTRACT

The absorption wavelength (λ_{\max}) of various representative dyes (indigo, azobenzene, phenylamine, hydrazone, anthraquinone, naphthoquinone, and cationic dyes) were calculated and compared by the INDO/S and the CNDO/S methods. Although calculated λ_{\max} values by both the INDO/S and the CNDO/S methods always underestimated the observed values, the INDO/S method reproduced the observed λ_{\max} value more correctly than the CNDO/S method in all the dyes examined. Neither method appears to be as predictively reliable as the PPP method for typical planar π -chromophore systems.

1 INTRODUCTION

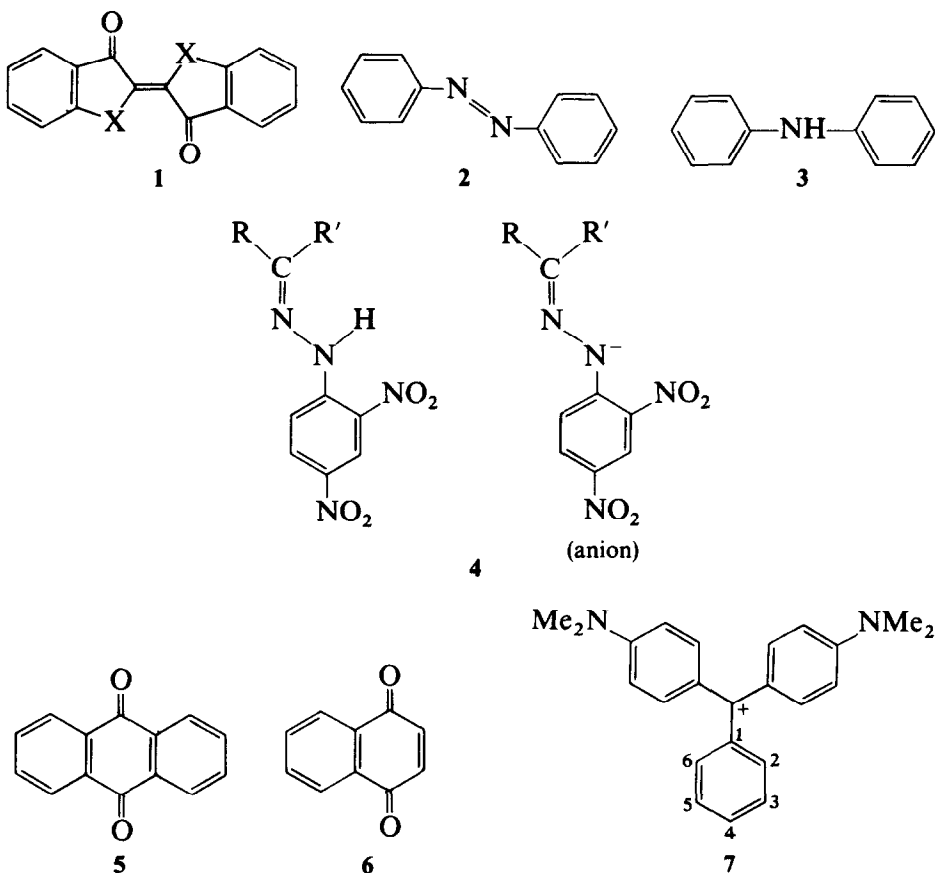
The effective design of organic functional dyes is one area where experimental synthesis and theoretical prediction can effectively interact.^{1–3} Usually the λ_{\max} calculation of dyes and pigments has been carried out using the Pariser–Parr–Pople (PPP) molecular orbital (MO) method,^{4,5} which has been proved to be very useful. However, the PPP method was originally designed for planar π -electron systems, neglecting all σ -electrons, and it is difficult to apply to non-planar systems, molecules containing hydrogen bonds, or to $n-\pi^*$ transitions. In order to treat such molecules, the CNDO/S method^{6,7} has been developed and some applications of it^{8,9} have been presented, although the results still remain to be improved.

We have therefore evaluated the validity³ of the CNDO/S method and the

more elaborate INDO/S method.¹⁰⁻¹² We have calculated data for representative dyes by both methods and compared the results with experimental data. This present paper reports the results of these comparisons.

2 CALCULATIONS

We selected typical and important systems in the organic dye chemistry, such as indigo (1), azobenzene (2), phenylamine (3), hydrazone (4), anthraquinone (5), naphthoquinone (6) and cationic dyes (7). Within each group, three to five different structures were used, and the λ_{\max} and oscillator strength calculated by the INDO/S and the CNDO/S methods were obtained.



The geometries of each molecule (indigo,¹³ azobenzene,¹⁴ phenylamine,¹⁵ hydrazone,¹⁶ anthraquinone,¹⁷ naphthoquinone¹⁸ and cationic dyes¹⁹)

TABLE 1
The Options of the INDO/S and the CNDO/S Calculations

<i>Option</i>	<i>INDO/S</i>	<i>CNDO/S</i>
Electronic repulsion	Nishimoto-Mataga ^c	Nishimoto-Mataga
β	Del Bene, Jaffe ^d	Del Bene, Jaffe
CI	196 conf. (S-CI) ^a	192 conf. (S-CI) ^b

^a {(HOMO-13) to HOMO} \times {LUMO to (LUMO + 13)}.

^b Selected small ΔE orbital.

^c Refs 22, 23.

^d Refs 6, 7.

were adopted from X-ray data. For the derivatives of each system, functional groups were replicated by using the standard bond lengths and angles.²⁰

The INDO/S program is provided by Zerner and the CNDO/S program is the QCPE-174 CNDO/S program.²¹ The options of the calculation were ordered to be as compatible as possible in the two methods (Table 1).

3 RESULTS AND DISCUSSION

The observed λ_{\max} and values calculated by the INDO/S and the CNDO/S methods are shown for indigo dyes in Table 2, for azobenzene dyes in Table 3, for phenylamine dyes in Table 4, for hydrazone dyes in Table 5, for

TABLE 2
The Observed and Calculated λ_{\max} of Indigo Dyes 1

<i>X</i>	<i>Observed</i>		<i>INDO/S</i>		<i>CNDO/S</i>	
	λ_{\max} (nm)	$\log \epsilon$	λ_{\max} (nm)	f^a	λ_{\max} (nm)	f^a
NH	605 ^{b,d}	4.22	474.6	0.617	376.2	0.632
O	420 ^{c,e}	4.08	342.6	0.284	295.3	0.281
NMe	650 ^{c,f}	4.13	608.4	0.398	463.4	0.372

^a Oscillator strength.

^b Solvent (CHCl₂)₂.

^c Solvent CHCl₃.

^d Ref. 24.

^e Ref. 25.

^f Ref. 26.

TABLE 3
The Observed and Calculated λ_{\max} of Azobenzene Dyes 2

Substituents	Observed ^a		INDO/S		CNDO/S	
	λ_{\max} (nm)	$\log \epsilon$	λ_{\max} (nm)	f^b	λ_{\max} (nm)	f^b
None	318 ^c	4.33	306.0	1.058	302.8	1.083
2-NH ₂	417 ^d	3.8	351.7	0.432	323.2	0.649
4-NEt ₂ , 4'-NO ₂	490 ^c	4.56	381.8	1.195	346.9	1.237
4-NEt ₂ , 2',4',6'-triCN	562 ^e	4.67	382.9	0.977	358.1	1.005

^a Solvent C₂H₅OH.^b Oscillator strength.^c Ref. 27.^d Ref. 28.^e Ref. 29.

anthraquinone dyes in Table 6, for naphthoquinone dyes in Table 7, and for cationic dyes in Table 8.

As shown in Tables 2 to 8, the values of the calculated λ_{\max} by both the INDO/S and the CNDO/S method are at lower wavelength compared with the observed values.

The reason for this could be that in both methods the original parameters were adjusted in order to reproduce small aromatic molecules,^{6,7,10-12} the absorptions of which were scarcely in the visible region.

Unless we attempt to parameterize for the visible region, a procedure which would require the modification of the entire scheme of the semi-empirical method, the important point in considerations of defining dye

TABLE 4
The Observed and Calculated λ_{\max} of Phenylamine Dyes 3

Substituents	Observed ^{a,c}		INDO/S		CNDO/S	
	λ_{\max} (nm)	$\log \epsilon$	λ_{\max} (nm)	f^b	λ_{\max} (nm)	f^b
2-NO ₂	425	3.89	392.9	0.139	318.6	0.135
4-NO ₂	393	4.43	330.1	0.512	276.1	0.376
2,4-diNO ₂	353	4.21	326.7	0.426	281.3	0.289

^a Solvent C₂H₅OH.^b Oscillator strength.^c Ref. 30.

TABLE 5
The Observed and Calculated λ_{\max} of Hydrazone Dyes 4

<i>R</i>	<i>R'</i>		Observed ^d		INDO/S		CNDO/S	
			λ_{\max} (nm)	$\log \epsilon$	λ_{\max} (nm)	f^c	λ_{\max} (nm)	f^c
H	H	Neutral ^a	345	4.32	349.2	0.554	297.5	0.511
H	H	Anion ^b	430	4.24	404.0	0.703	384.0	0.639
			500	4.02	508.9	0.464	444.0	0.370
<i>p</i> -NO ₂ C ₆ H ₄	CH ₃	Neutral ^a	382	4.54	354.5	0.805	307.0	0.809
<i>p</i> -NO ₂ C ₆ H ₄	CH ₃	Anion ^b	540	4.57	548.1	0.611	473.8	0.742
<i>p</i> -NH ₂ C ₆ H ₄	CH ₃	Neutral ^a	403	4.43	365.3	0.674	313.0	0.667
<i>p</i> -NH ₂ C ₆ H ₄	CH ₃	Anion ^b	461	4.42	435.2	1.002	416.2	0.914

^a Solvent CHCl₃ (neutral).

^b C₂H₅OH containing NaOH (anion).

^c Oscillator strength.

^d Ref. 31.

parameters prior to synthesis is not the absolute values, but the reproducibility of the qualitative properties of dyes.

The observed λ_{\max} and the λ_{\max} calculated by the INDO/S method are shown in Fig. 1 and by the CNDO/S method in Fig. 2. The straight lines in Figs 1 and 2 were evaluated by the least squares method and the λ_{\max} relationship between the observed λ_{\max} and those calculated by the INDO/S method was

$$\lambda_{\max}(\text{obs}) = 1.65 \lambda_{\max}(\text{calc}) - 187(\text{nm}) \quad (1)$$

Correlation coefficient 0.604

TABLE 6
The Observed and Calculated λ_{\max} of Anthraquinone Dyes 5

Substituents	Observed ^{a,c}		INDO/S		CNDO/S	
	λ_{\max} (nm)	f^b	λ_{\max} (nm)	f^b	λ_{\max} (nm)	f^b
1-NH ₂	465	0.114	340.4	0.190	296.5	0.148
2-NH ₂	410	0.091	312.6	0.105	283.2	0.042
1,4-diNH ₂	550	0.157	389.9	0.243	324.1	0.213
2-NMe ₂	470	0.109	329.2	0.147	288.1	0.060
1-OH	405	0.113	308.9	0.163	285.4	0.211

^a Solvent CH₂Cl₂.

^b Oscillator strength.

^c Ref. 32.

TABLE 7
The Observed and Calculated λ_{\max} of Naphthoquinone Dyes 6

Substituents	Observed ^d		INDO/S		CNDO/S	
	λ_{\max} (nm)	$\log \epsilon$	λ_{\max} (nm)	f^a	λ_{\max} (nm)	f^a
5-OMe	387	3.56 ^b	364.9	0.145	322.0	0.154
5-NH ₂	484	3.73 ^b	415.8	0.175	340.9	0.163
5-NH ₂ , 8-OMe	512	3.60 ^b	440.3	0.216	365.6	0.202
2,3-diCl, 5-NH ₂ -8-OMe	540	3.80 ^b	452.1	0.224	—	—
2,3-diCN, 4-NH ₂	585	3.61 ^c	444.5	0.189	366.1	0.158

^a Oscillator strength.^b Solvent cyclohexane.^c Solvent benzene.^d Ref. 33.

and that by the CNDO/S method

$$\lambda_{\max}(\text{obs}) = 2.31 \lambda_{\max}(\text{calc}) - 334(\text{nm}) \quad (2)$$

Correlation coefficient 0.498

The relationship between the observed molar extinction coefficient (ϵ) and the INDO/S calculated oscillator strength (f) is shown in Fig. 3 and that for the CNDO/S method in Fig. 4.

Although both the INDO/S and the CNDO/S methods seem to be useful

TABLE 8
The Observed and Calculated λ_{\max} of Cationic Dyes 7

Substituents	Observed ^a		INDO/S		CNDO/S	
	λ_{\max} (nm)	$\log \epsilon$	λ_{\max} (nm)	f^b	λ_{\max} (nm)	f^b
None	612 ^c	5.02	457.3	0.821	392.5	0.713
	427.5	4.30	393.0	0.583	354.5	0.572
4-CN	643 ^d	4.94	461.2	0.828	401.3	0.711
	429	4.20	400.7	0.679	361.6	0.684
4-Cl	657 ^e	4.91	500.6	0.845	—	—
3,5-diNO ₂	431	4.15	401.1	0.539	—	—

^a Solvent 98% CH₃COOH.^b Oscillator strength.^c Ref. 34.^d Ref. 35.^e Ref. 36.

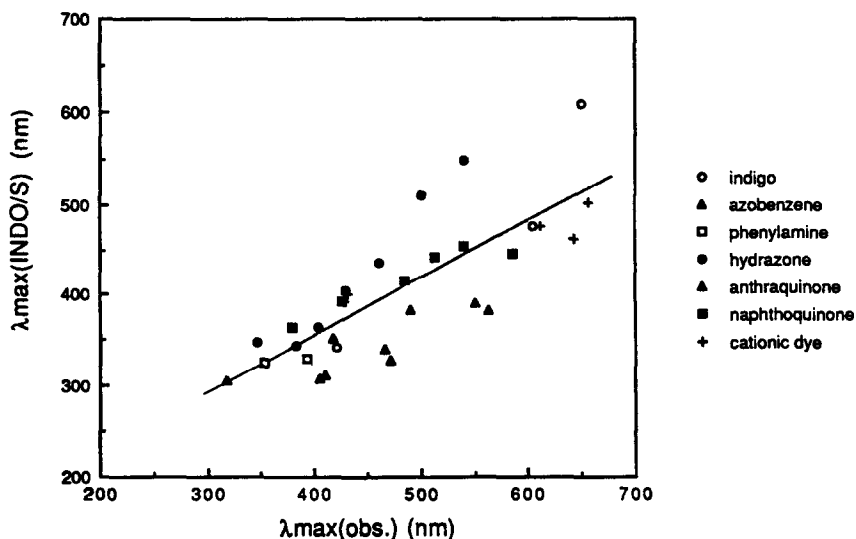


Fig. 1. The relationship between the observed and the INDO/S calculated λ_{\max} value.

for qualitative reproduction of the experimental absorption, the results shown in Figs 1 and 2 and the above relationships (1) and (2) indicate the superiority of the INDO/S method over the CNDO/S method. In order to investigate this further, we carried out the CNDO/S calculation using the INDO/S parameter set (ionization potential, (ss/ss) integral value, β value); the results of the CNDO/S calculation thus obtained were found to be almost of the same order. We thus conclude, with respect to the superiority

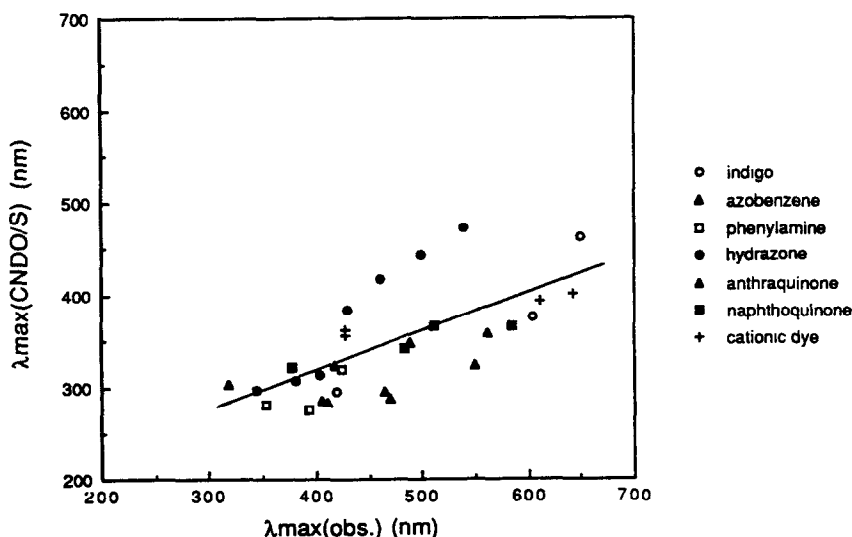


Fig. 2. The relationship between the observed and the CNDO/S calculated λ_{\max} value.

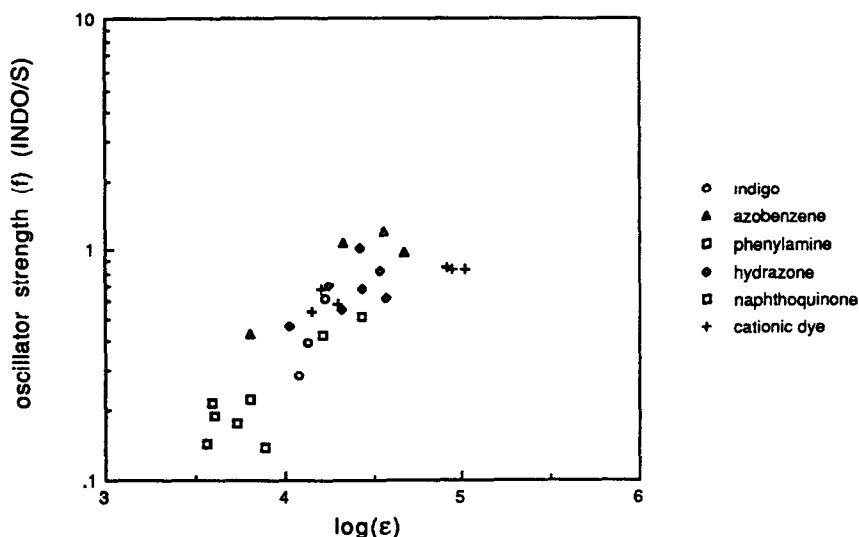


Fig. 3. The relationship between the observed molar extinction coefficient (ϵ) and the INDO/S calculated oscillator strength (f).

of the INDO/S method, that the inclusion of one-center exchange repulsion integrals is an improvement for the absorption wavelength reproduction.

The results of calculated oscillator strengths are shown in Fig. 3 (INDO/S) and in Fig. 4 (CNDO/S), together with the observed molar extinction coefficients. Both methods gave similar results, which implies that both are useful for the prediction of the experimental absorption strength.

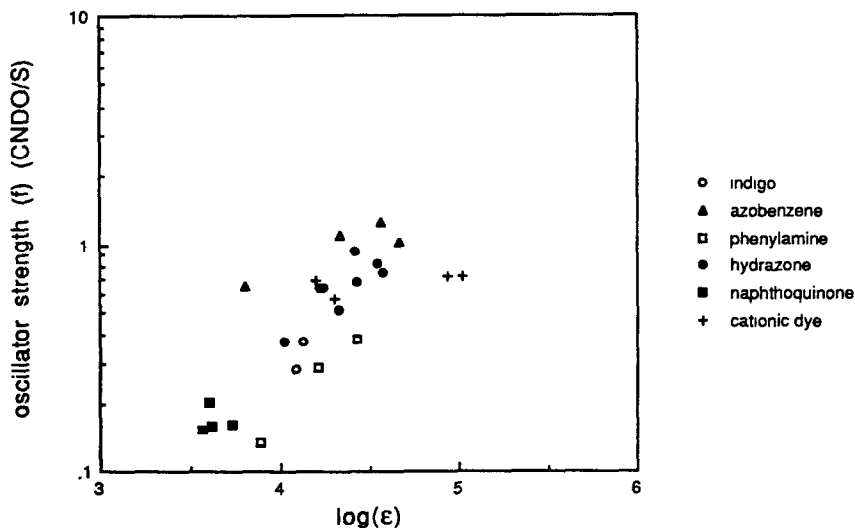


Fig. 4. The relationship between the observed molar extinction coefficient (ϵ) and the CNDO/S calculated oscillator strength (f).

4 CONCLUSION

Calculations of the λ_{\max} for seven typical organic dye systems using the INDO/S and the CNDO/S methods have been made. Both methods were shown to be useful for dye design and for qualitative reproduction of the λ_{\max} and oscillator strength. With respect to absorption strength, both methods gave similar results, but for λ_{\max} the INDO/S method was somewhat better than the CNDO/S method. Neither method had the predictive reliability of the PPP method for the planar π chromophores studied here. However, we note the utility of the CNDO/S and the INDO/S methods for nonplanar molecules and $n-\pi^*$ transitions,³ where the predictive capability was determined to be better than that found here.

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