On the Induced Optical Activity of Triphenylmethane Dyes

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INDO/S calculations applied to the skewed benzaurin chromophore reveal large rotational strength associated with the lowest electronic excited states. The calculated oscillator and rotational strengths are compared with the experimental data for induced optical activity of sulphonephthalein-cinchona alkaloid complexes.

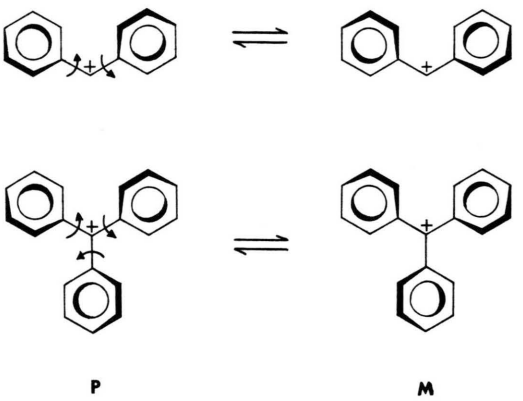
Introduction

Induced circular dichroism (ICD) of Bromophenol Blue and Tetraiodofluorescein in lactic dehydrogenase solutions has been observed by Towell and Woody and interpreted in terms of exciton coupling between dye molecules and dye conformational changes [1].

Recently we have reported on remarkable ICD within sulphonephthalein absorption bands, in complexes with chiral aminoalcohols, such as cinchona alkaloids [2]. While analytical applications of this sensitive spectroscopic method still remain to be elaborated, we have addressed the question of the origin of the induced optical activity in triphenylmethane dyes.

It has been shown by X-ray analysis that the triphenylmethyl carbonium ion in perchlorate or fluorborate is nonplanar, with the three phenyl rings forming propeller blades and with the three central carbon atom-phenyl ring bonds being coplanar. The dihedral angle (the skew angle) between the central plane and individual phenyl ring planes has been found to be 31.8° ± 0.6° [3]. Non-planar conformations have been calculated by Hoffmann for diphenylmethyl and triphenylmethyl cations [4]. Thus, the di- and triphenylmethyl cations exist in solution in equilibrium of P and M helicity molecules (Scheme 1), their interconversion being performed by conrotatory ring motion [4].

Common to all phthalein and sulphonephthalein dyes is the benzaurin chromophore. In order to assess the effect of conformation on the rotatory power of benzaurin we performed INDO/S calculations on the twisted benzaurin chromophore and compared the results with the available experimental data for ICD of sulphonephthalein-alkaloid complexes.



Scheme 1

Results and Discussion

The calculations were carried out using the spectroscopically parameterized semiempirical INDO/S method [5]. The molecular coordinates were calculated from idealized models (vide infra). Excited state wavefunctions were constructed from the ground state orbitals, including all singly excited configurations with excitation energies up to 10 eV (about 180–200 configurations). Despite the zero differential overlap approximation incorporated in the INDO/S method the oscillator and rotational strengths were calculated including all one- and two-center contributions [6]. The electric transition

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moments were evaluated within the dipole velocity formalism.

The INDO/S calculations were applied to the following structures (Scheme 2): protonated benzaurin (**1a, 1b**), benzaurin (**2a**), deprotonated benzaurin (**3a, 3b**) and fuchsone (**4a**). Dipolar forms (**2b** and **4b**) were not taken into consideration.

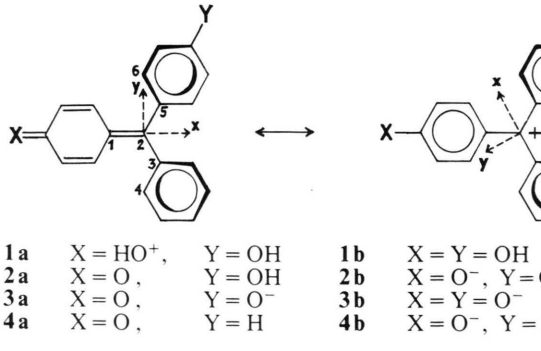
For the calculations the coordinates were chosen to keep C_2 symmetry for the structures **1b, 3b** and **4a.** The bond lengths (in Å) were selected as follows:

Quinoid ring		Phenyl ring	
C1–C2	1.36	C2–C3 and C2–C5	1.45
C–C	1.48	C⁼C	1.40
C=C	1.32	C–O	1.38
C=O	1.22	O–H	1.00
		C–H 1.09	

The bond angles were 120°, except for C–O–H (107.6°). The two phenyl rings were twisted in a conrotatory manner with respect to the third one (quinoid ring in **1a–4a,** Scheme 2), so that the dihedral angles C1–C2–C3–C4 and C1–C2–C5–C6 were +30° each. The dipole velocity formalism was used in calculating the electric transition moments. Representative calculations in the dipole length formalism for **2a** and **4a** gave qualitatively comparable results for the lowest energy excited states.

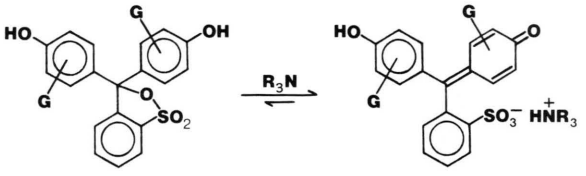
The results of the calculations are collected in Table 1. The transitions with both dipole and rotational strength below ± 0.15 are not quoted.

The benzaurin chromophore (**2a**) is the chromophore of sulphonephthaleins deprotonated with one equivalent of base (Scheme 3). The observed lowest lying absorption maximum of the benzaurin chromophore in sulphonephthaleins (410 ± 10 nm, $\varepsilon = 2 \cdot 10^4$) [2] corresponds to the calculated x-polarized transitions 1 and 2 of **2a** at 397 and 361 nm (dipole strength 0.19 and 0.48, respectively). For the assumed twist angle +30° the rotational strengths



1a	X = HO^+,	Y = OH	**1b**	X = Y = OH	
2a	X = O,	Y = OH	**2b**	$X = O^-$,	Y = OH
3a	X = O,	$Y = O^-$	**3b**	$X = Y = O^-$	
4a	X = O,	Y = H	**4b**	$X = O^-$,	Y = H

Scheme 2



Scheme 3

Table 1. INDO/S calculated positions λ (in nm), dipole strengths D (in square Debye), and rotational strengths R (in Debye-Bohr magneton) for electronic transitions in **1a–4a** skewed at +30 degrees. For **1b, 3b** and **4a** the symmetries of the excited states are given in parentheses.

	λ	D	R		λ	D	R
1a				**1b**			
1	423	0.68	0.70	1(B)	397	0.73	−0.09
2	360	0.34	0.47	2(A)	364	0.58	−0.57
3	343	0.03	−0.26	3(B)	338	0.02	0.35
4	272	0.02	0.19	4(A)	329	0.07	0.74
5	244	0.22	1.07	5(B)	306	0.01	0.57
6	242	0.08	0.29	6(B)	207	0.22	4.81
7	223	0.03	1.15	7(A)	201	0.18	−0.83
8	218	0.03	0.50	8(A)	200	0.27	−0.57
3a				**3b**			
1	509	0.51	0.50	1(B)	541	0.70	0.41
2	361	0.01	0.31	2(A)	390	0.02	−0.32
3	345	0.01	0.30	3(A)	376	0.39	0.48
4	311	0.37	0.03	4(A)	320	0.04	−0.30
5	301	0.03	0.21	5(B)	318	0.16	0.29
6	293	0.19	−0.41	6(B)	252	0.02	−0.37
7	251	0.06	0.54	7(B)	249	0.13	0.60
8	246	0.07	−0.48	8(A)	231	0.01	0.21
				9(B)	217	0.09	0.56
				10(B)	213	0.02	0.57
				11(B)	211	0.04	0.23
				12(A)	210	0.42	−1.18
2a				**4a**			
1	397	0.19	1.56	1(A)	445	0.02	0.90
2	361	0.48	−0.81	2(A)	366	0.50	−0.73
3	281	0.44	0.68	3(B)	278	0.32	0.64
4	253	0.15	−0.72	4(A)	256	0.18	−0.10
5	251	0.10	−0.45	5(B)	241	0.07	2.59
6	241	0.05	2.40	6(A)	231	0.01	0.50
7	228	0.02	0.29	7(B)	226	0.02	0.31
8	225	0.03	0.39	8(A)	223	0.20	−0.68
9	223	0.14	−0.24	9(A)	219	0.13	−0.91
				10(B)	215	0.43	0.24
				11(A)	213	0.13	0.42
				12(A)	206	0.07	−0.51

calculated for transitions 1 and 2 are strongly positive ($R = 1.56$) and negative ($R = -0.81$), respectively. The two lowest energy ICD maxima of Bromothymol Blue with cinchonine ($\Delta\varepsilon = +7.5$ at 435 nm and -0.2 at 378 nm) [2] correspond qualitatively to the calculated values, but no quantitative comparison of the calculated and observed rotatory strengths is possible – primarily due to the lack of data on the equilibrium between the P and M helicity dyes in the diastereomeric alkaloid complexes.

A third transition is calculated at 281 nm (dipole strength 0.44) and may correspond to the experimental band in sulphonephthaleins at ca. 310 nm ($\varepsilon < 10^4$). The rotational strength of the third band is calculated to be positive, although weaker ($R = 0.68$) compared to the first transition. This is the case in the Bromothymol Blue – cinchonine complex, the observed $\Delta\varepsilon$ value being +6.3 at 337 nm [2].

The remaining calculated transitions of **2a** between 253 and 223 nm cannot be correlated with the experimental data and are not further discussed.

The correlation of the calculated oscillator and rotational strengths of **2a** with the ICD data for sulphonephthalein-cinchonine complexes is further supported by an extension of the calculations of the excited states to **2a** with the C1–C2–C3–C4 and C1–C2–C5–C6 angles set at +15°, +22.5°, +45°, +60°, and +75°.

The results, summarized in Fig. 1, reveal the presence of the three lowest energy transitions, as previously found for the skew angle +30°. The energy of the excited states rises with increasing nonplanarity of the benzaurin chromophore. The second transition has an opposite rotational strength with respect to the transitions 1 and 3. The highest rotational strength is associated with transition 1, which appears to reach the maximum at a skew angle $\approx +30°$. On the other hand, transition 2 has a high dipole strength, gradually rising with the nonplanarity of the chromophore.

The removal of the OH group in **2a** leads to the fuchsone chromophore (**4a**). Because of C_2-symmetry, the excited states of **4a** have either A or B symmetry (Table 1), the calculated two lowest lying states having A-symmetry. Transition 1(A) at 445 nm has low dipole strength and high positive rotational strength, while 2(A) at 366 nm is characterized by high dipole strength and negative rotational strength. A similar pattern of transitions has been calculated for **2a** at the skew angle +30° and suggests that both benzaurin and fuchsone belong to the same π-electron chromophoric system. Predictably, the B-state 3(B) in **4a** is of higher energy than the A-state.

Distinct transitions have been calculated for both **2a** and **4a** at 241 nm, characterized by low oscillator strength and high positive rotational strength – not accessible, however, for experimental identification.

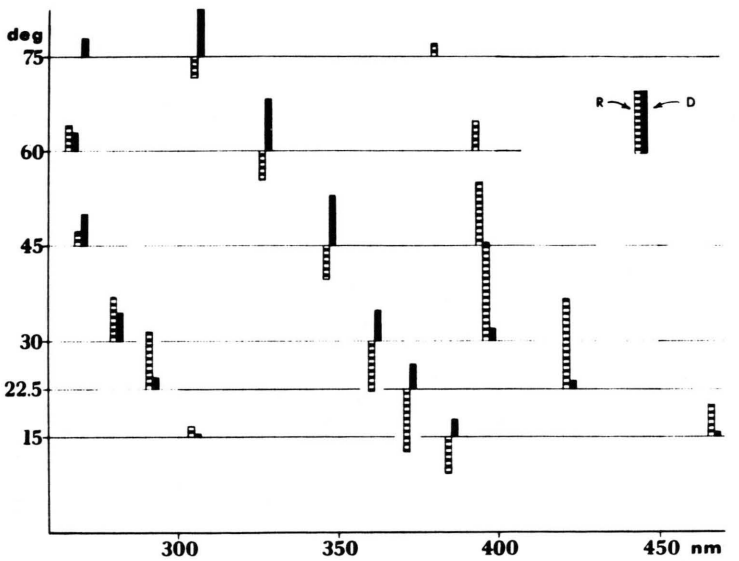


Fig. 1. Positions, dipole strengths D (in square Debye), and rotational strengths R (in Debye-Bohr magneton) for the three lowest energy transitions in **2a** calculated with the skew angle ranging from 15° to 75°.

Turning now to the protonated benzaurin chromophore **1a, b** (Scheme 2) we find that the lowest energy transition in **1a** is *x*-axis polarized while that in **1b** is of B-symmetry, thus *y*-axis polarized. The first two allowed transitions calculated for **1a** have positive rotational strength, while those of **1b** have negative rotational strength. This result strongly indicates the importance of the structural parameters chosen for calculating the rotatory power. To test further this effect we have calculated the dipole and rotational strengths of **1b,** using bond lengths and bond angles determined for triphenylmethyl perchlorate by X-ray studies [3] and assuming a twist angle +30° (Table 2).

Table 2. Results of INDO/S calculations (as in Table 1) using bond lengths and bond angles as determined by X-ray data for triphenylmethyl perchlorate [3] and the skew angle +30°.

	λ	D	R		λ	D	R
1b				**3b**			
1	399	0.79	0.13	1	540	0.75	0.46
2	364	0.68	−0.30	2	412	0.00	−0.16
3	315	0.11	0.31	3	371	0.46	0.30
4	299	0.01	0.63	4	316	0.17	0.29
5	205	0.10	2.23	5	306	0.04	−0.38
				6	299	0.00	−0.23
				7	288	0.05	0.38

Comparison of Tables 1 and 2 reveals that the first two transitions of **1b** at ca. 400 nm and 365 nm are calculated to be strongly allowed for both sets of parameters, but the calculated rotatory strength for the lowest energy transition is again changed from negative to positive.

No experimental data for the ICD of protonated benzaurin derivatives are available at present.

The deprotonated benzaurin chromophore can again be considered in the two mesomeric forms **3a** and **3b** (Scheme 2). As expected, the first transition is red-shifted in **3b** at 540 nm, and strongly allowed. In **3b** the lowest energy state has B-symmetry with the corresponding transition being *y*-axis polarized.

Both structures **3a** and **3b** are calculated to give positive rotational strengths ($R = 0.50$ and 0.41, respectively) for the lowest energy transition at the skew angle +30°. An additional calculation for **3b** using bond lengths and bond angles as determined by X-ray data for the triphenylmethyl cation [3] leads again to the lowest lying transition at 540 nm, with positive rotational strength ($R = 0.46$).

The calculated position of the low energy transition of **3b** can be matched well with the position of the lowest transition from PPP calculation for Malachite Green (**3b,** X = Y = NMe_2) [7].

The structures corresponding to **3b** are obtained by deprotonation of easily ionized sulphonephtha-

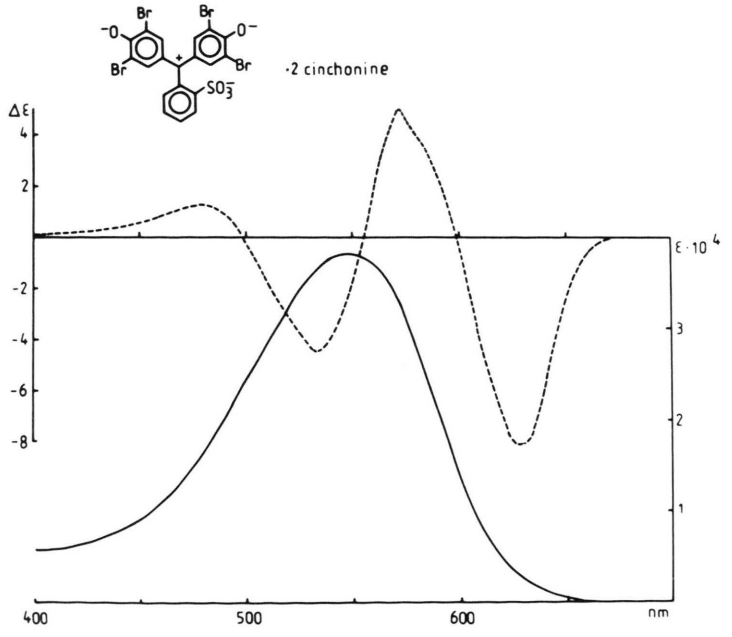


Fig. 2. ICD (---) and electronic spectrum (——) of the Bromophenol Blue ($4 \cdot 10^{-5}$ M) – cinchonine ($1 \cdot 10^{-4}$ to $8 \cdot 10^{-4}$ M) complex in benzene. The ICD baseline was recorded with a solution of Bromophenol Blue – diazabicyclooctane complex.

lein dyes, such as Bromophenol Blue and Bromocresol Green, in complexes with amines. An example of Bromophenol Blue dianion formed with at least 2 molar equivalents of cinchonine, is shown in Figure 2.

The observed absorption band at ca. 550 nm corresponds well to the calculated position of the transition to the lowest B-state in **3b.** The recorded ICD spectrum is quite complex, however, and it consists of four bands of alternating sign, the lowest energy one being negative. The broad 550 nm band of Bromophenol Blue-cinchonine is thus composed of two or more bands, contrary to the calculation on the simple benzaurin anion. According to INDO/S calculations (Table 1 and 2) the next transition is located around 400 nm and is of negative rotational strength. Thus the experimental results indicate that in case of Bromophenol Blue (and similar dye complexes) the simple theoretical prediction for the symmetrically skewed benzaurin anion model is not adequate.

Other sources of ICD may lie in the interactions between two or more dye molecules. However, under conditions of our measurements the formation of dye dimers is improbable, as it requires polar solvents, low temperatures and high concentrations. Still another possibility is the exciton type interaction between allowed transitions of the dye chromophore and the amine chromophore. Such an interaction should be more evident in the ICD of **2a,** whose low-energy transition lies closer to the allowed transitions of the quinoline chromophore in cinchonine. However no exciton type curve is seen in the ICD spectra of sulphonephthalein monoanions [2].

It should be emphasized that the electronic structure of the Bromophenol Blue chromophore is more complex than the benzaurin model. Also the conformation of the dye in the complex with chiral amine is very likely to be different from the symmetrical skewed benzaurin model.

In conclusion we note that our INDO/S calculations for the benzaurin chromophore predict satisfactorily the position of the lowest energy absorption bands in neutral and deprotonated molecules and that positions of the bands are not much different from those in the series of sulphonephthalein dyes. The ICD of sulphonephthalein anions in complexes with chiral amines can be traced to the skewed benzaurine model (**2a**), but the ICD of sulphonephthalein dianions is not satisfactorily reproduced by the skewed benzaurin anion model (**3a, 3b**). Clearly additional experimental ICD data on simple benzaurin/fuchsone chromophores are needed for better understanding optical rotatory power of these molecules.

Acknowledgement

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