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Studies of the circular dichroism spectra of dissymmetric Schiff-bases by means of the exciton chirality method

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Abstract

The circular dichroism spectra of some dissymmetrical Schiff-bases derived from condensation of 2 mol salicylaldehyde with 1 mol of a chiral diamine are analyzed in terms of a simple conformational model taking the angle between the aromatic chromophores as a variable. The rotatory strengths of the $\pi\rightarrow\pi^*$ transitions are calculated with AM1 molecular orbitals in combination with the dipole-coupling approximation. Calculated CD curves are found to be in reasonable agreement with the experimental CD spectra. Differences in the CD spectra of the Schiff-bases are discussed in relation to variation of the theoretical CD curve of ethylenebis(salicylideneimine) as a function of conformation. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Recently, Schiff-base ligands, particularly dissymmetric saldiamine derivatives, have received much attention because some of their transition metal complexes are efficient catalysts for a variety of enantioselective reactions.[1–9] Circular dichroism spectra are relevant for the characterization of chiral quadridentate Schiff-bases because they provide insights into conformations of the bases as well as conformational changes upon chelation with a metal ion.[6,10] We have previously reported the synthesis and characterization of Schiff-base ligands derived from the condensation of 2 mol of 5-X-salicylaldehyde (X is OCH_3, H, Br or NO_2) with (1*S*,2*S*)-diphenyl-1,2-diaminoethane.[11] Except for differences in the frequencies of the CD bands due to electronic effects of 5,5′-substituents, the CD spectra of the above compounds, in chloroform or dichloromethane, are rather similar. Interestingly, such spectra differ in shape and sign sequence from those of analogous Schiff-bases derived from condensation of 2 mol of salicylaldehyde with (1,2*S*)-diaminopropane, (2*S*,3*S*)-diaminobutane or (1*S*,2*S*)-diaminocyclohexane.[12] These differences are ascribed, in part, to contributions of the exciton coupling of the B_{2u} $\pi\rightarrow\pi^*$ transitions of the phenyl substituents at positions 8,8′.[11,12] However, deviations from the 60° staggered $\Lambda\delta$

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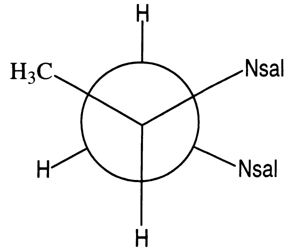
conformation, due to differences in the bulk of the 8,8′-substituents, would also change the CD spectra. In spite of their dissimilarities, the CD sign patterns of all of these saldiamine derivatives indicate a preference for a $\Lambda\delta$ conformation, i.e. a positive chirality. On the other hand, except for the 1*S*,2*S*-diaminocyclohexane derivative, formation of copper(II) chelates with all the ligands occurs with changes in the sign patterns of the CD spectra. Such modifications indicate that these ligands change conformation upon chelation, which results in predominance of a $\Delta\lambda$ conformation.[11,12] Instead, for the 1*S*,2*S*-diaminocyclohexane derivative the positive chirality of the ligand is maintained in the respective copper(II) chelate due to the conformational requirements imposed by two fused rings.[12] We used the molecular exciton theory[13] to investigate effects of conformational changes on the CD spectrum of the ethylenebis(salicylideneimine) system. Results were used to account for differences in the shape and sign sequence of the CD spectra of the saldiamine Schiff-bases derived from 1,2*S*-diaminopropane **1**, (1*S*,2*S*)-diaminocyclohexane **2**, (2*S*,3*S*)-diaminobutane (**3**) and (1*S*,2*S*)-diphenylethylenediamine **4**.



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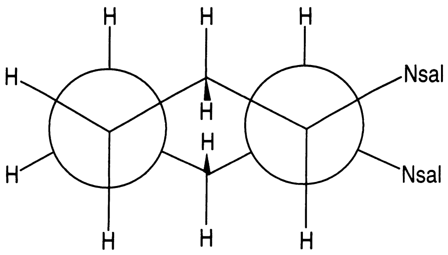

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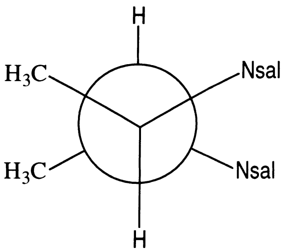

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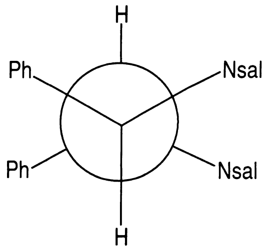

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METHOD OF CALCULATION

The salicylaldimine was the model for the salicylideneimine chromophore. Molecular orbital calculations were made using the AM1 method.[14] We verified the reliability of the resulting energy levels for studying the electronic spectra with molecular orbital calculations on 5-methoxy and 5-bromosalicylaldimine. The virtual orbital approximation was used for constructing the excited states. Electronic excitations involving the two highest occupied and the three lowest unoccupied π MO's of salicylaldimine were considered. Thus, the electric dipole transitions which were assumed to contribute to the UV spectrum were $\Psi_0 \rightarrow \Psi_{5,6}$, $\Psi_0 \rightarrow \Psi_{4,6}$, $\Psi_0 \rightarrow \Psi_{5,7}$ and $\Psi_0 \rightarrow \Psi_{5,8}$, where subscript 0 indicates the fundamental state and subscripts 4–8 refer to the single occupied π MO's in the excited state, in a sequence of increasing energy. According to previous designations[11] these transitions are denoted as $\pi_0 \rightarrow \pi_1^*$, $\pi_{-1} \rightarrow \pi_1^*$, $\pi_0 \rightarrow \pi_2^*$ and $\pi_0 \rightarrow \pi_3^*$, respectively.

Electric dipole transition moments were calculated, except for $\pi_0 \rightarrow \pi_3{}^*$ which was not accessible in the CD spectra. For each transition, the center of charge of the low-energy single occupied MO in the excited state was chosen as the origin in defining the respective dipole transition moment. Both one-center and two-center transition integrals over atomic orbitals were considered. The $S(2p_{\pi a},2p_{\pi b})$, $(81a_0/8\mu_a)S(2p_{\pi a},3d_{\pi b})$ and $(81a_0/8\mu_b)S(2p_{\pi a},3d_{\pi b})$ type two-center integrals appearing in expressions for the electric dipole moment integrals were evaluated with the appropriate master formulas[15,16] by using Slater atomic orbitals. The transition moments thus calculated were further corrected by a factor of 0.332, corresponding to a correction factor of 0.11 for the interaction energies, V_{0a12} and the rotational strengths, R_{0a}.[17] This factor was estimated from the ratio $f(\pi_0 \rightarrow \pi_L{}^*)$(exp.)/$f(\pi_0 \rightarrow \pi_L{}^*)$(theor.), where $f(\pi_0 \rightarrow \pi_L{}^*)$ denotes the oscillator strength of the absorption band centered at 313 nm in the electronic spectrum of the 1,2*S*-diaminopropane derivative.[12] The interaction energies between the salicylideneimine chromophores were calculated by means of the dipole–dipole approximation.[13] Only interactions between identical transitions were considered. As a starting point the salicylideneimine moieties were assumed to lie in planes which define a dihedral angle ϕ about the C–C bond of the ethylene group. The interaction energy as a function of ϕ was formulated according to the coordinate system given in Fig. 1. The local coordinate systems are equivalent under C_2 symmetry and the following expression was derived:

$$V_{oa12} = (\mu_{yoa}{}^2\cos\phi - \mu_{xoa}{}^2)/(R_{12})^3 + 3\,[X\mu_{xoa} + Y\mu_{yoa}(1-\cos\phi)]^2/(R_{12})^5 \qquad (1)$$

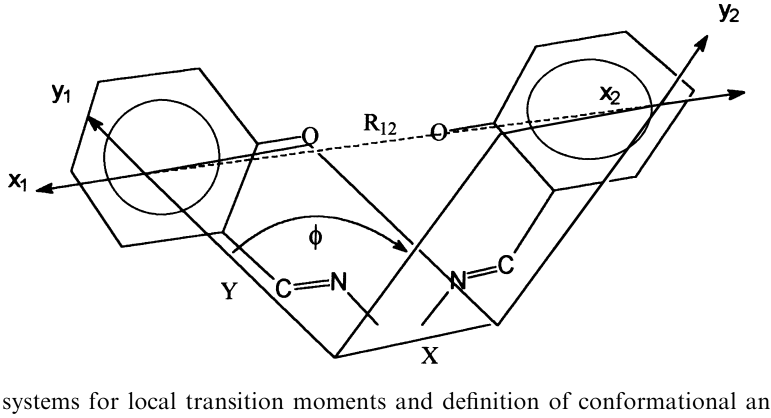


Figure 1. Coordinate systems for local transition moments and definition of conformational angle ϕ. The z_1 and z_2 axes have been omitted because directions of polarization lie in x_1,y_1 and x_2y_2 planes only

where 1 and 2 indicate the salicylideneimine chromophores, $\mu_{x0a} = \mu_{x0a1} = \mu_{x0a2}$ and $\mu_{y0a} = \mu_{y0a1} = \mu_{y0a2}$ are components of the electric dipole moments of the $\Psi_0 \rightarrow \Psi_a$ local transitions along the x_1 or x_2 and y_1 or y_2 axes, respectively, X is the distance between the origins of the transition moments at $\phi = 0$, Y is the distance from the origin of the transition moment to the rotation axis, and R_{12} is the distance between the origins of the transition moments as a function of ϕ, i.e.

$$R_{12} = [2\,Y^2(1-\cos\phi) + X^2]^{1/2}$$

In terms of the coordinate system shown in Fig. 1, the general expression for the exciton rotational strengths[13] leads to the following equation:

$$R_{oa} = \pm\ \pi\,(1/\lambda_a)\,[\,(Y\,\mu_{xoa}\,\mu_{yoa} - (X/2)\,\mu_{yoa}^{2})\,]\,\sin\phi \tag{2}$$

where the signs correspond to the in-phase and out-of-phase coupling modes, respectively, λ_a is the wavelength of the $\Psi_0 \rightarrow \Psi_a$ transition of the monomeric chromophore, and the remaining terms have been defined. If torsions preserving the C_2 symmetry are also considered about the C(8)–N and C(8′)–N′ bonds Eqs. (1) and (2) will still be valid, but parameters X and Y will depend on ϕ.

Circular dichroism curves were calculated by using the approximation[18]

$$\pm\,|\,\Delta\varepsilon_{oai}\,| \approx 2.464\,(10^{38})\,R_{oai}\,\lambda_{ai}/\Delta_{ai} \tag{3}$$

where i denotes a specific band of the exciton couplet, $|\ \Delta\varepsilon_{0ai}\ |$ is the absolute maximum of the excitonic CD band i of the $\Psi_0 \rightarrow \Psi_a$ transition, R_{0ai} is the rotational strength calculated from Eq. (2), λ_{ai} is the CD maximum for the excitonic band, i, and Δ_{ai} is the band width. If V_{0a12} is expressed in wave numbers

$$\lambda_{ai} = \lambda_a / (\lambda_a V_{oa12} \pm 1)$$

where i denotes the sign which is in the denominator, viz. negative for the in-phase and positive for the out-of-phase coupling mode, and the experimental value of λ_a is taken. Simulations of CD spectra were made by using the expression

$$\Delta\varepsilon(\lambda) = \Sigma_{ai}\{\,\Delta\varepsilon_{oai}\exp[\,-(1/\Delta_{ai})^{2}(\lambda_{ai} - \lambda)^{2}]\,\} \tag{4}$$

which involves the summation of six Gaussian excitonic CD bands. Both ϕ and Δ_{ai} values were iterated until theoretical and experimental CD curves were similar in shape and sign patterns. For comparative purposes, theoretical CD curves were further scaled by empirical factors calculated as $\Delta\varepsilon_L$ (exp.)/$\Delta\varepsilon_L$ (theor.), where $\Delta\varepsilon_L$ indicates the maximum of the lower-energy CD band of the respective Schiff-base. Electronic spectra were also calculated for some selected ϕ values by using the approximation

$$\varepsilon(\lambda) = \kappa\varepsilon'(\lambda) = \kappa\,\Sigma_{ai}\{\,[\,\lambda_{ai}(\mu_{oa})^{2}/(\lambda_a\Delta_{ai})\,]\exp[\,-(1/\Delta_{ai})^{2}(\lambda_{ai} - \lambda)^{2}]\,\} \tag{5}$$

which involves the summation of six Gaussian absorption bands. In the above expression subscript oa stands for $\Psi_0 \rightarrow \Psi_a$, $(\mu_{0a})^2 = (\mu_{x0a})^2 + (\mu_{y0a})^2$, λ_{ai} is the wavelength at the maximum optical density for a particular excitonic band (ai), λ_a is the wavelength of the transition $\Psi_0 \rightarrow \Psi_a$ of the monomeric chromophore, Δ_{ai} is the band width and κ is an empirical factor calculated as the ratio ε_L (exp)/ε_L' (theor), where ε_L refers to the maximum optical density for the lower-energy absorption band.

2. Results and discussion

Good linear correlations were found between the AM1 π-MO energy differences for salicylaldimine and its 5-bromo and 5-methoxy derivatives and the corresponding frequencies of the $\pi_0 \rightarrow \pi_1^*$, $\pi_0 \rightarrow \pi_2^*$ and $\pi_0 \rightarrow \pi_3^*$ transitions of the respective Schiff-bases derived from ethylenediamine (Table 1). A similar result was obtained for the correlation between the AM1 π-MO energy differences for salicylaldimine and the frequencies of the $\pi_0 \rightarrow \pi_1^*$, $\pi_0 \rightarrow \pi_2^*$ and $\pi_0 \rightarrow \pi_3^*$ transitions of the 1,2-diphenylethylenediamine derivatives, viz. $y = 7.143x - 30.323$, $r = 0.9997$. Thus, this relationship was used to estimate the frequency of the $\pi_{-1} \rightarrow \pi_1^*$ transition for Schiff-base **4**. For compounds **1**, **2** and **3** the frequency of the $\pi_{-1} \rightarrow \pi_1^*$ transition was estimated by using regression equations with the same slope as that obtained for the correlation between the AM1 π-MO energy differences for salicylaldimine and the π→π* frequencies of ethylenebis(salicylideneimine) (Table 1).

Table 1

Correlation of AM1 π-MO energy differences for salicylaldimine and its 5-OCH_3 and 5-Br derivatives with experimental energies of the π→π* transitions (in wave numbers) of the respective Schiff-bases derived from ethylenediamine[a]

Transition	$\pi_0 \rightarrow \pi_1^*$	$\pi_{-1} \rightarrow \pi_1^*$	$\pi_0 \rightarrow \pi_2^*$	$\pi_0 \rightarrow \pi_3^*$
Salicylaldimine				
x = AM1 Δε (eV)	8.631	9.530	9.626	10.347
y = 1 / λ_a (kK) (exp.)[a]	31.447	-	38.911	43.668
1 / λ_a (kK) (calc.)[b]	31.552	37.975	38.661	43.813
λ_a (nm) (exp.)[a]	318.0	-	257.0	229.0
λ_a (nm) (calc.)[b]	316.9	263.3	258.7	228.2
Regression equation: $y = 7.145x - 30.117$; $r = 0.9994$				
5-methoxysalicylaldimine				
x = AM1 Δε (eV)	8.070	9.525	9.192	9.835
y = 1 / λ_a (kK) (exp.)[a]	28.818	-	38.760	42.735
1 / λ_a (kK) (calc.)[b]	29.082	40.714	38.052	43.193
λ_a (nm) (exp.)[a]	347.0	-	258.0	234.0
λ_a (nm) (calc.)[b]	343.9	245.6	262.8	231.5
Regression equation: $y = 7.995x - 35.438$; $r = 0.9962$				
5-bromosalicylaldimine				
x = AM1 Δε (eV)	8.517	9.573	9.325	9.751
y = 1 / λ_a (kK) (exp.)[a]	30.211	-	39.370	43.668
1 / λ_a (kK) (calc.)[b]	30.292	41.864	39.150	43.819
λ_a (nm) (exp.)[a]	331.0	-	254.0	229.0
λ_a (nm) (calc.)[b]	330.1	238.9	255.4	228.2
Regression equation: $y = 10.962x - 63.071$; $r = 0.9996$				

[a] From ref. 11.

[b] Calculated with the appropriate regression equation.

The eigenvectors of the AM1 π-MO considered for assigning transitions of the salicylideneimine chromophore are listed in Table 2, where atoms have been labelled as in Fig. 2. These data show that transitions $\pi_0\rightarrow\pi_1^*$, $\pi_{-1}\rightarrow\pi_1^*$ and $\pi_0\rightarrow\pi_2^*$ involve the salicylideneimine chromophore as a whole. Such a result disagrees with assignments of the bands of the electronic spectra of saldiamines given earlier, which ascribed the absorption band centered near 318 nm to a $\pi\rightarrow\pi^*$ transition localized mainly on the azomethine chromophore.[12,19] For ethylenebis(salicylideneimine) the respective AM1 π-MO energies and correlation equation (Table 1) indicate that $\pi\rightarrow\pi^*$ transitions, mainly localized on the azomethine chromophore, should appear at wavelengths below 170 nm.

Table 2

Eigenvectors of the AM1 π-MO selected for assigning the $\pi\rightarrow\pi^*$ transitions of salicylideneimine chromophore

Atom labelling[a]	π_{-1}	π_0 (HOMO)	π_1^*(LUMO)	π_2^*	π_3^*
C(1)	-0.4682	0.3758	0.3416	-0.0153	0.3472
C(2)	0.0054	0.3915	-0.2593	0.5535	-0.0301
C(3)	0.4876	0.3807	-0.2799	-0.3784	-0.2918
C(4)	0.4603	-0.1384	0.4546	-0.1180	0.4195
C(5)	-0.0138	-0.5071	-0.0359	0.5177	-0.2512
C(6)	-0.4599	-0.2183	-0.4142	-0.4661	-0.0518
C(7)	0.1012	-0.0127	0.4059	-0.0667	-0.5969
N	0.3286	-0.2122	-0.4242	0.0635	0.4420
O	-0.0355	-0.4375	0.1163	-0.2062	0.0046

[a] According to Fig. 2.

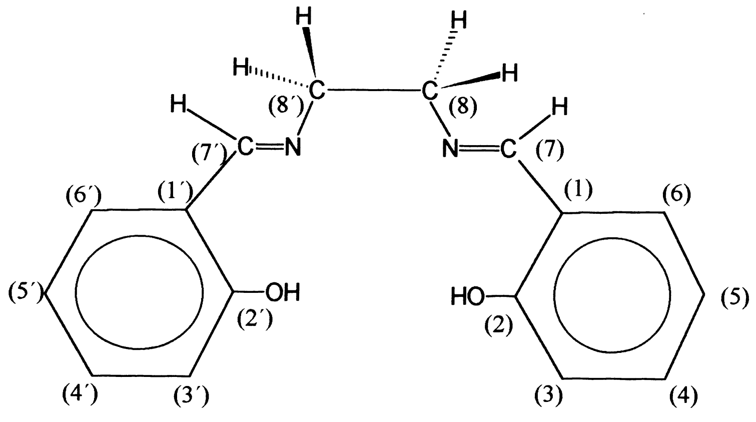


Figure 2. Atom labelling of ethylenebis(salicylideneimine)

Electric transition moments calculated from the eigenvectors listed in Table 2 are shown in Table 3 together with other parameters involved in Eqs. (1) and (2). These data show that the direction of polarization of the transition $\pi_0 \rightarrow \pi_1^*$ is at ca. 75° from the x axis, i.e. at ca. 86° from the azomethine bond. In turn, directions of polarizations of transitions $\pi_{-1} \rightarrow \pi_1^*$ and $\pi_0 \rightarrow \pi_2^*$ are at ca. 32° and 30° from the x axis, respectively.

Table 3
Electric-dipole moments of $\pi \rightarrow \pi^*$ transitions of salicylideneimine chromophore and other parameters involved in the expressions for the interaction energy (Eq. (1)) and rotational strength (Eq. (2))

	$\pi_o \rightarrow \pi_1^*$	$\pi_{-1} \rightarrow \pi_1^*$	$\pi_o \rightarrow \pi_2^*$
$1 / \lambda_a$ (kK)	31.25[a]	(37.75)[b]	38.61[a]
	31.92[c]	(38.52)[b]	39.39[c]
μ_x (eA)[d]	0.192	0.865	-0.719
μ_y (eA)[d]	-0.715	0.548	-0.416
X (A)[e]	5.622	6.306	5.622
Y (A)[e]	3.938	3.876	3.938

[a] Values for ligands 5-6 in ref. 11.

[b] Calculated from correlation between AM1 π-MO energy differences and experimental frequencies of $\pi \rightarrow \pi^*$ transitions.

[c] Estimated from ref. 12.

[d] Corrected by the factor 0.332 (see the text). A = angstrom

[e] Calculated from an idealized geometry. A = angstrom

Selected values of interaction energies and rotatory strengths are listed in Tables 4 and 5. These data show that, because of the different directions of polarization of the $\pi \rightarrow \pi^*$ transitions, for a particular value of ϕ the interaction parameter calculated for the transition $\pi_0 \rightarrow \pi_1^*$ is considerably smaller than those for the transitions $\pi_{-1} \rightarrow \pi_1^*$ and $\pi_0 \rightarrow \pi_2^*$, while the inverse occurs with the absolute values of the rotational strengths. Thus, in predicting CD spectra the effects of differences in exciton splitting and rotatory strength offset each other so that the summation curve in the region of the transition $\pi_0 \rightarrow \pi_1^*$ results in a similar amplitude to that in the region of transitions $\pi_{-1} \rightarrow \pi_1^*$ and $\pi_0 \rightarrow \pi_2^*$.

Values of the empirical scale factor $\Delta\varepsilon_L$ (exp.)/$\Delta\varepsilon_L$ (theor.) are 3.68, 2.63, 1.91 and 0.75 for Schiff-bases **1**, **2**, **3** and **4**, respectively. The cases where $\Delta\varepsilon_L$ (exp.)/$\Delta\varepsilon_L$ (theor.) > 1 reflect the fact that rotations about the N–C(8) and N′–C(8′) bonds have not been explicitly considered in the conformational model. Nevertheless, if the C_2 symmetry is preserved, such additional torsional angles should affect all interacting transitions similarly. In turn, both $\Delta\varepsilon_L$ (exp.)/$\Delta\varepsilon_L$ (theor.) < 1 for compound **4** and the different values in $\Delta\varepsilon_L$ (exp.)/$\Delta\varepsilon_L$ (theor.) among the remaining Schiff-bases reflect the fact that the systems are equilibrium mixtures of conformers.[12]

Table 4
Interaction energies (cm^{-1}) of the ethylenebis(salicylideneimine) system for some selected ϕ values

ϕ (degrees)	$V_{12}(\pi_o \rightarrow \pi_1^*)$	$V_{12}(\pi_{-1} \rightarrow \pi_1^*)$	$V_{12}(\pi_o \rightarrow \pi_2^*)$
15	338.4	795.9	739.8
29	249.0	714.4	634.8
34	214.8	678.9	591.3
50	121.3	561.6	456.4

Table 5
Absolute values of rotatory strength (erg cm^3) of the system ethylenebis(salicylideneimine) for some selected ϕ values[a]

ϕ (degrees)	$\lvert R(\pi_o \rightarrow \pi_1^*) \rvert$	$\lvert R(\pi_{-1} \rightarrow \pi_1^*) \rvert$	$\lvert R(\pi_o \rightarrow \pi_2^*) \rvert$
15	1.157×10^{-38}	0.634×10^{-38}	0.500×10^{-38}
29	2.214×10^{-38}	1.204×10^{-38}	0.956×10^{-38}
34	2.553×10^{-38}	1.389×10^{-38}	1.102×10^{-38}
50	3.498×10^{-38}	1.903×10^{-38}	1.510×10^{-38}

[a] $\lvert R_{oa} \rvert$ values of 15° were calculated with frequency data from ref. 11 whereas those of 29, 34 and 50° were calculated with data from ref. 12.

Band widths of ca. 31 nm were required for simulating the sign patterns of the CD spectra. Therefore, Gaussian exponents for Eq. (4) were in the range $0.98 \times 10^{-3} \geq (1/\Delta)^2 \geq 1.07 \times 10^{-3}$. Such band width requirements might also be reflecting the fact that our conformational model is applied to diastereomeric mixtures. In turn, band widths of 18 nm were necessary for simulating the electronic spectra.

Theoretical electronic and CD spectra generated from the parameters given in Tables 4 and 5 are shown in Figs. 3 and 4, where experimental literature data are included for purposes of comparison. As shown in Figs. 3 and 4, the theoretical and experimental electronic spectra agree in both positions and relative values of the optical density maxima. Small deviations are observed, however, for the minima at 283 nm (Fig. 3) and at 290 nm (Fig. 4), because they appear bathochromically shifted by 7 and 6 nm in the corresponding theoretical spectra, respectively. These discrepancies might be due to overestimation of the exciton splitting of the $\pi_{-1} \rightarrow \pi_1^*$ transitions.

The theoretical and experimental CD curves of Schiff-bases **1**, **2** and **3** (Fig. 3) match in both sign patterns and relative amplitudes of the bands. However, the positive bands at 323–326 and 264–267 nm in the experimental spectra are bathochromically shifted by 8–12 and 7–10 nm, respectively, in the theoretical spectra. Moreover, the negative CD bands at 239–248 nm in the experimental spectra are hypsochromically shifted by 6–14 nm in the theoretical spectra. However, these deviations fall within the range often observed in theoretical calculations.[20–22] A

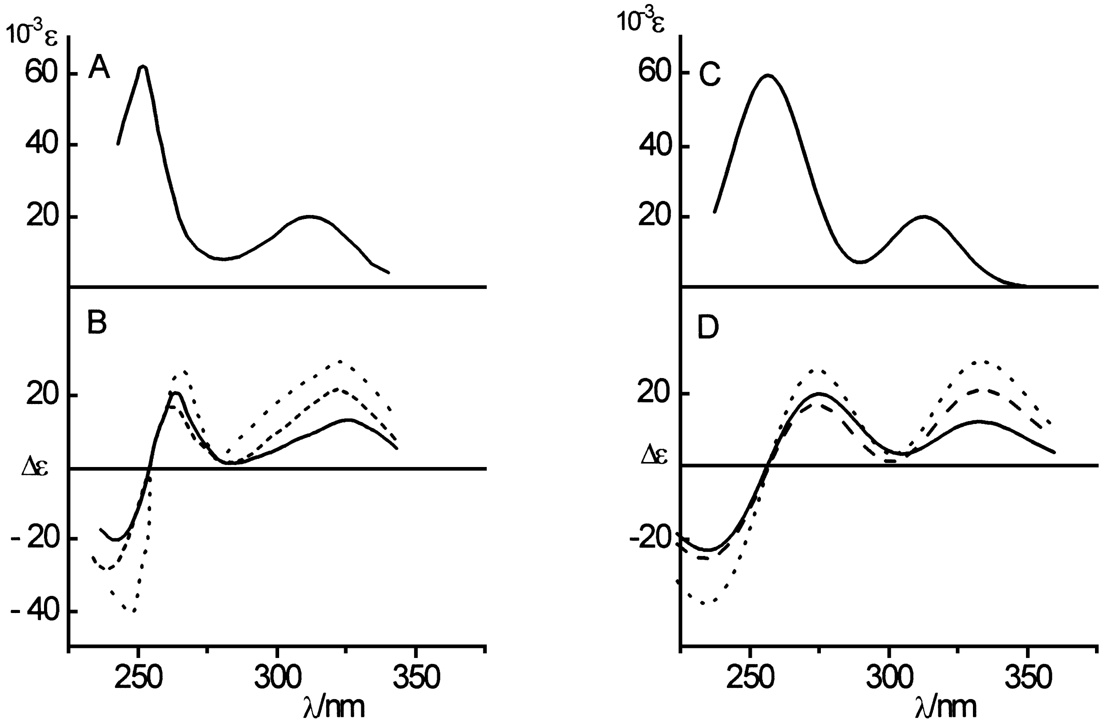


Figure 3. (A) Electronic spectrum of Schiff-base **1** in chloroform solution; (B) CD spectra of Schiff-bases **1** (—), **2** (····) and **3** (- - -); in chloroform solution (from Ref. 12); (C) theoretical electronic spectrum for ϕ = 50°; (D) theoretical CD curves for ϕ = 50° (—), 34° (····) and 29° (- - -)

more serious deviation in the theoretical spectra (Fig. 3) is the bathochromic shift by ca. 22 nm of the experimental minimum at ca. 280 nm. The probable origin of these discrepances is that the dipole–dipole approximation overestimates the interaction energies.

The theoretical and experimental CD curves of Schiff-base **4** (Fig. 4) match acceptably in both sign pattern and relative intensities of the bands at 251, 303 and 332 nm. However, the positive band near 280 nm has, in the theoretical spectrum, an amplitude ca. 5.5 times greater than that observed. Such a discrepancy would arise from the contributions of the exciton coupling between the transitions B_{2u} of phenyl substituents on C(8) and C(8′), which are arranged according to a negative chirality, being neglected in our calculations.[11,12] Furthermore, discrepancies could also arise because contributions of mixed exciton coupling between $\pi_{-1}\rightarrow\pi_1{}^*$ and $\pi_0\rightarrow\pi_2{}^*$ transitions of the salicylideneimine moiety and the B_{2u} transitions of the phenyl chromophores are neglected. The positive band at 332 nm in the experimental spectrum of **4** is bathochromically shifted by 9 nm in the theoretical spectrum, and the negative band at 251 nm is hypsochromically shifted by 13 nm (Fig. 4). Such deviations are typical in theoretical calculations.[20–22]

As shown in Tables 4 and 5 and Fig. 3, ϕ values of 50, 34 and 29° were necessary to generate CD curves agreeing in both relative band amplitudes and sign patterns with the experimental CD spectra of Schiff-bases **1**, **2** and **3**, respectively, and a ϕ value of 15° was required for compound **4** (Tables 4 and 5 and Fig. 4). Such ϕ values appear to be unreasonable because, at least for Schiff-base **2**, $\phi\approx60°$ is expected. However, we note that, in neglecting torsions about bonds N–C(8) and N′–C(8′), our iterative procedure used for predicting the CD spectrum of a particular Schiff-base should lead to a ϕ value reflecting the angle between the molecular planes of the chromophores

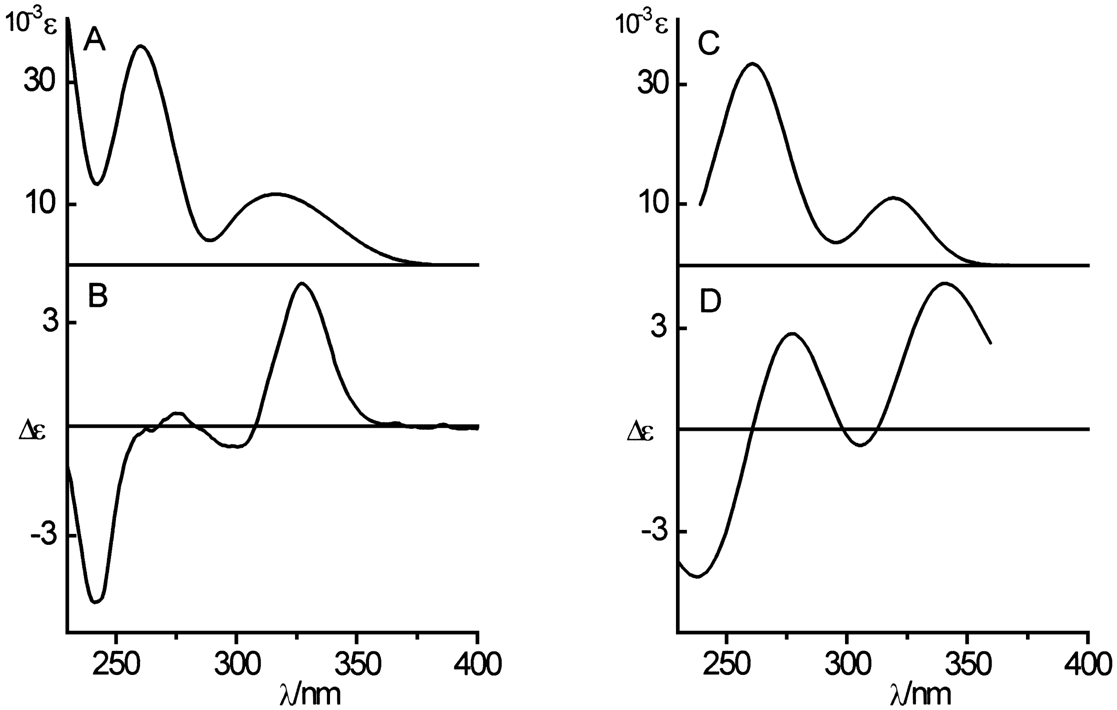


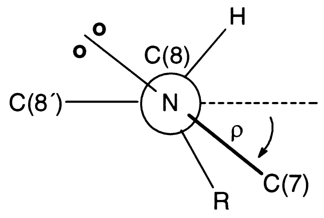
Figure 4. (A) Electronic spectrum and (B) CD spectrum of Schiff-base **4** in dichloromethane solution; (C) theoretical electronic spectrum and (D) CD curve for $\phi = 15°$

rather than the actual N–C(8)–C(8′)–N′ torsion angle in the prevailing equilibrium conformation. Instead, different requirements for ϕ among the Schiff-bases reflect changes in the N–C(8)–C(8′)–N′ torsion angle because the C(8′)–C(8)–N–C(7) and C(8)–C(8′)–N′–C(7′) torsion angles should be equivalent under C_2 rotation and similar among these compounds.

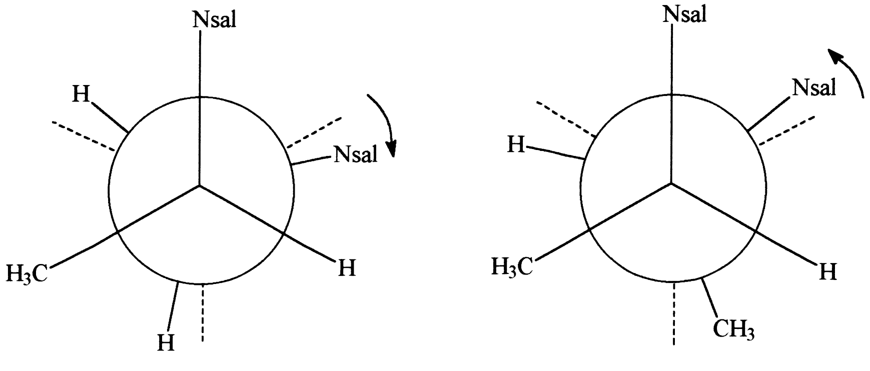
Geometrical considerations indicate that:

$$\sin[(\psi - \phi)/2] \approx (8 + \sin^2\rho)^{-1/2} \sin\rho$$

where ψ is the N–C(8)–C(8′)–N′ torsional angle, ϕ is the angle between the molecular planes of the chromophores and ρ is the C(8′)–C(8)–N–C(7), or C(8)–C(8′)–N′–C(7′) torsional angle. If a value of 60° is assumed for the torsion angle ψ in compound **2**, use of $\phi = 34°$ gives a clockwise value of ca. 40° for ρ, which is reasonable in view of repulsions between the lone pairs on the nitrogen atoms and the C(8)–C(8′) bond.



Thus, if we assume that $\rho = 40°$ for the remaining Schiff-bases, the torsion angle ψ should be 76, 55 and 41° for compounds **1**, **3** and **4**, respectively. Such a sequence can be correlated with variations of repulsions between substituents on the ethylene moiety through the series. Thus, for compound **1** repulsions between the salicylideneimine moieties should prevail over those between hydrogen atoms on C(8) and the methyl group on C(8′), making $\psi > 60°$ (Fig. 5). In turn, for compound **3** repulsions between the methyl groups on C(8) and C(8′) should be predominant because the distance between the methyl groups is smaller than that between the bulks of the salicylidene moieties. Thus, for compound **3** the CH_3–C(8)–C(8′)–CH_3 torsion angle should be $> 60°$ and, therefore, $\psi < 60°$ (Fig. 5). There should be a similar but stronger effect in compound **4** because of the bulk phenyl substituents on C(8) and C(8′), which fits the obtained sequence of ϕ (or ψ) values.



(1) (3)

Figure 5. Newman projections along the C(8)–C(8′) bond in Schiff-bases **1** and **3**

In summary, our results show that differences in the shape and sign pattern of the CD spectra of the ethylenebis(salicylideneimine) derivatives arise mainly from variations in the N–C(8)–C(8′)–N′ torsion angle of the dominant $\Lambda\delta$ conformer rather than from differences in the conformational equilibria. This last factor, instead, should be a determinant for the observed amplitude differences in the CD spectra.

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