Optically Active Amines. 27.[1] CNDO/S Calculations on the Azomethine and Conjugated Azomethine Chromophores[2]

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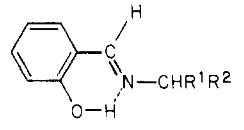
Quantum mechanical calculations using the CNDO/S–CI method on methylenimine, benzylidenimine, and salicylidenimine give transition energies for the respective $\pi \rightarrow \pi^*$ transitions in agreement with the strong absorption bands observed in their respective electronic absorption spectra. The calculated polarization direction of band II in benzylidenimine and salicylidenimine near 248 and 255 nm, respectively, is almost parallel to the benzene ring–methine carbon bond and conforms to the observation that Cotton effects associated with band II for the *N*-benzylidene, *N*-salicylidene, and *N*-*o*-methoxybenzylidene derivatives of a particular chiral amine all have the same sign. The polarization direction of band I in salicylidenimine at 300 nm, although not entirely parallel to the benzene ring–methine carbon bond, has its larger component along this bond. This points to the possibility, however, of sign differences for the Cotton effects associated with bands I and II as is sometimes observed in the circular dichroism spectra of chiral salicylidenimino derivatives. The calculations also indicate that, in the CD spectra of the *N*-salicylidene derivative of some chiral amines, the CD maximum near 275 nm, between bands I and II and of opposite sign to that of these two bands, is correctly assigned to the n $\rightarrow \pi^*$ transition of the conjugated azomethine group.



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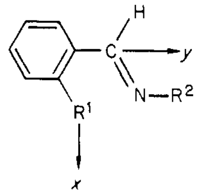
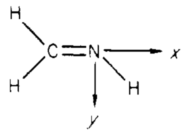
The salicylidenimino chirality rule[4] has been successfully applied to correlate the circular dichroism (CD) spectra of the *N*-salicylidene derivatives (1) of a variety of chiral amines[4-10] with the absolute configuration of the chiral center to which the nitrogen atom is attached. This was made possible by the realization that the CD bands at about 315 and 255 nm, referred to as bands I and II, respectively, have electric transition moments roughly parallel to the benzene ring–methine carbon bond of the salicylidenimino chromophore and that the dominant contribution of the associated Cotton effects is that of the coupled oscillator mechanism,[11] resulting in the same sign for both bands. Previous assignments for the transition moment directions were based mainly on the physcial perception of the chromophore excited states[12] rather than on hard experimental or theoretical evidence. Furthermore, there are some cases, although infrequent, in which CD bands I and II differ in sign[7] and others in which there is the appearance of an additional CD maximum near 275 nm different in sign from that of bands I and II.[1,7-10] This band, on the basis of CD spectral evidence,[1] was deduced as being associated with the n $\rightarrow \pi^*$ transition of the azomethine group occurring at about 240 nm.[13] That this band appears near 275 nm was attributed to a considerable red shift due to conjugation with the benzene ring, partially offset by a blue shift as the result of intramolecular hydrogen bonding in the salicyidenimino chromophore (1).

Consequently, a molecular orbital calculation on salicylidenimine (2) was made to put the assigned transition energies and the transition moment directions of the salicylidenimino chromophore on a firmer theoretical ground. To facilitate the calculation for 2, similar calculations were first made on methylenimine (3) and benzylidenimine (4). The CNDO/S–CI method[14] was chosen since it has been demonstrated to give good spectral results, especially for compounds containing nonbonding electrons.[15]



2, R^1 = OH; R^2 = H
4, R^1 = R^2 = H
5, R^1 = H; R^2 = CH_3



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Results and Discussion

Two sets of parameters were used in the CNDO/S calculations and are tabulated in Table I. The original parametrization[14] is designated as A while the revised set[15] is designated as B. Since the polarization direction of a transition is of interest for CD studies, the polarizations of the electric transition moments were calculated in addition to the oscillator strengths for the transitions. The magnetic transition moments are perpendicular to the

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[1] Part 26: H. E. Smith, B. G. Padilla, J. R. Neergaard, and F.-M. Chen, *J. Org. Chem.*, **44**, 1690 (1979).

[2] Supported by National Science Foundation Grant No. CHE77-24293.

[3] (a) Vanderbilt University; (b) Tennessee State University; supported by National Science Foundation Grant No. CHE77-04608.

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Table I. Parameters Used in CNDO/S Calculations

		atom[a]			
	electron	H	C	N	O
slater exponents		1.2	1.625	1.95	2.275
core integrals, eV	s	14.35	28.10 (29.92)	38.63 (40.97)	50.78 (54.51)
	p		11.14 (11.61)	14.55 (16.96)	18.22 (21.93)
repulsion integrals (Γ_{rr}), eV		12.85	11.11 (10.93)	12.01 (11.88)	13.0 (15.13)
resonance integrals (β_r^0), eV		−12.0	−17.00 (−17.5)	−26.0	−45.0

[a] Values not in parentheses are those of original parametrization in ref 14 which is designated A. Values in parentheses are later alternate values in ref 15 and when used the parametrization is designated B.

Table II. Results of CNDO/S Calculations for Methylenimine (3)

	transition						
				moment[a]			
				electric, D			
c	type	wavelength, nm	oscillator strength	*x*	*y*	*z*	magnetic, μ_B
A (11[b])	$\sigma(n) \rightarrow \pi^*$	311.2	0.005			−0.57	1.06
	$\pi \rightarrow \pi^*$	138.8	0.588	−4.14	−0.45		0.06
	$\sigma \rightarrow \pi^*$	136.7	<0.001			−0.09	1.12
	$\pi \rightarrow \sigma^*$	134.5	0.029			−0.91	0.12
	$\sigma(n) \rightarrow \sigma^*$	117.4	0.135	−1.48	1.09		0.92
A (20)	$\sigma(n) \rightarrow \pi^*$	311.9	0.006			−0.60	1.06
	$\pi \rightarrow \pi^*$	157.7	0.413	−3.71	−0.23		0.10
	$\sigma \rightarrow \pi^*$	136.7	<0.001			−0.11	1.12
	$\pi \rightarrow \sigma^*$	134.5	0.029			−0.91	0.12
	$\sigma(n) \rightarrow \sigma^*$	119.1	0.082	−1.18	0.84		0.85
A (30)	$\sigma(n) \rightarrow \pi^*$	311.9	0.006			−0.60	1.06
	$\pi \rightarrow \pi^*$	167.0	0.391	−3.72	−0.22		0.04
	$\sigma \rightarrow \pi^*$	136.9	<0.001			−0.11	1.12
	$\pi \rightarrow \sigma^*$	134.5	0.029			−0.91	0.12
	$\sigma(n) \rightarrow \sigma^*$	120.3	0.056	−0.88	0.81		0.78
B (11[b])	$\sigma(n) \rightarrow \pi^*$	297.2	0.004			−0.53	1.05
	$\pi \rightarrow \pi^*$	138.0	0.567	−4.05	−0.45		0.10
	$\sigma \rightarrow \pi^*$	136.3	<0.001			−0.12	1.12
	$\pi \rightarrow \sigma^*$	130.2	0.023			−0.80	0.18
	$\sigma(n) \rightarrow \sigma^*$	117.3	0.144	−1.56	1.08		0.92

[a] The origin is at the nitrogen atom. [b] Equal to the number of valance orbitals included. [c] Parametrization (no. of CI states used).

respective electric transition moments, and no symmetry designation is made since it is implicit in the electric transition moment direction. The electric transition moments were calculated by the dipole length method[15] while the magnetic transition moments were calculated by the method of Linderberg and Michl[16] which includes only one-center contributions.

Methylenimine (3). The coordinate system for methylenimine is shown in 3, with the origin taken to be at the nitrogen atom since the n → π^* transition of the imino chromophore is of primary interest. Distances for the C═N, C—H, and N—H bonds were taken as 1.24, 1.08, and 0.99 Å, respectively, and all bond angles were taken as 120°. Results of the CNDO/S calculation with both sets of parameters are given in Table II. No great difference is found for these two parametrizations using 11 configuration interaction (CI) states, this number of CI states being equal to the number of valance orbitals included. Results are also shown for calculations using larger numbers of CI states for parametrization A. It is interesting to note that only the $\pi \rightarrow \pi^*$ transition is sensitive to configuration interaction and improves steadily as more CI states are employed. For 30 CI states the $\pi \rightarrow \pi^*$ transition energy is calculated to be 167.0 nm, in good agreement with the experimentally observed absorption at 172–181 nm,[17] and is to be compared with 122 nm calculated by the ab initio method.[18] The calculated 311.9-nm $\sigma(n) \rightarrow \pi^*$ transition is at a decidedly longer wavelength than the 245-nm transition observed experimentally in alkylazomethines[13,17] and that of the ab initio calculation.[18] In contrast to the ab initio calculation, however, the CNDO/S calculation places the $\sigma(n) \rightarrow \sigma^*$ transition at a higher energy than that of the $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ transitions. No attempt was made to study the convergence of the CI expansions in more detail. It should be noted, however, that other studies indicate that the convergence of the CI expansions is very slow[19] and sometimes oscillatory.[20]

Benzylidenimine (4). The coordinate system for benzylidenimine is given in 4, the origin at the phenyl group attachment atom so chosen as to approximate the center of the benzylidenimino chromophore. The two different parametrizations A and B were again used. In addition, two different geometries were used. That with the C═N bond distance of 1.24 Å, the same as that in methylenimine (3), and the phenyl–C bond distance of 1.46 Å is referred to as geometry 1,[18] and that with the C═N and phenyl–C bond distances of 1.30 and 1.38 Å, respectively, is referred to as geometry 2.[21] For the benzene ring, the lengths for the C–C and C–H bonds were taken as 1.39 and 1.085 Å, respectively, for both geometries, and

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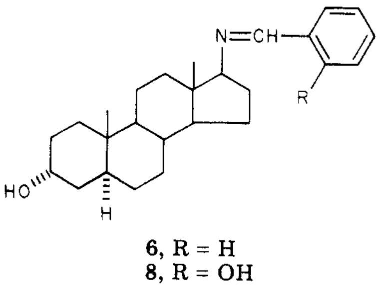
Table III. Results of CNDO/S Calculations Using Geometry 1

	transition						
				moment[a]			
				electric, D			magnetic, μ_B
compd[b,e]	type	wavelength, nm	oscillator strength	x	y	z	
benzylidenimine (4)[c] (A)	$\sigma(n) \rightarrow \pi^*$	322.1	0.004			0.55	0.99
	$\pi \rightarrow \pi^*$	272.0	<0.001	0.10	−0.10		0.02
	$\pi \rightarrow \pi^*$	230.0	0.441	−0.75	−4.58		0.34
	$\sigma \rightarrow \pi^*$	198.4	<0.001			0.02	0.35
	$\pi \rightarrow \pi^*$	195.2	0.540	3.80	−2.82		0.98
	$\sigma \rightarrow \pi^*$	193.7	<0.001			0.07	0.39
	$\pi \rightarrow \pi^*$	191.7	0.985	−4.11	−4.82		0.50
(B)	$\sigma(n) \rightarrow \pi^*$	306.9	0.004			0.51	0.96
	$\pi \rightarrow \pi^*$	264.9	0.003	0.37	−0.19		0.11
	$\pi \rightarrow \pi^*$	228.2	0.478	−0.83	−4.74		0.35
	$\sigma \rightarrow \pi^*$	195.5					0.25
	$\pi \rightarrow \pi^*$	193.4	0.510	4.10	−2.04		1.00
	$\sigma \rightarrow \pi^*$	191.1	<0.001			0.08	0.39
	$\pi \rightarrow \pi^*$	189.9	0.887	−3.40	−4.92		0.35
salicylidenimine (2)[d] (A) [O]	$\sigma \rightarrow \pi^*$	406.8	0.002			−0.40	0.33
	$\pi \rightarrow \pi^*$	324.6	0.189	−1.78	3.15		0.81
	$\sigma \rightarrow \pi^*$	254.7	<0.001			0.08	0.76
	$\pi \rightarrow \pi^*$	248.8	0.024	0.01	1.13		0.07
	$\sigma \rightarrow \pi^*$	238.2	0.004			0.43	0.43
	$\pi \rightarrow \pi^*$	227.3	0.019	0.67	0.70		0.12
	$\pi \rightarrow \pi^*$	216.2	1.15	4.15	5.95		0.35
(B) [O]	$\sigma \rightarrow \pi^*$	371.9	0.002			−0.38	0.32
	$\pi \rightarrow \pi^*$	313.0	0.194	−1.76	3.13		0.79
	$\pi \rightarrow \pi^*$	241.4	0.121	0.85	2.34		0.03
	$\sigma \rightarrow \pi^*$	232.0	<0.001			0.08	0.72
	$\pi \rightarrow \pi^*$	222.2	0.021	−0.55	−0.83		0.01
	$\sigma \rightarrow \pi^*$	221.4	0.004			0.41	0.40
	$\pi \rightarrow \pi^*$	210.4	1.031	3.70	5.69		0.33
(A) [N]	$\sigma \rightarrow \pi^*$	357.0	0.004			0.55	0.79
	$\pi \rightarrow \pi^*$	290.4	0.080	−1.01	1.97		0.51
	$\pi \rightarrow \pi^*$	241.0	0.139	−0.76	2.56		0.43
	$\sigma \rightarrow \pi^*$	212.4	0.001			0.16	0.85
	$\pi \rightarrow \pi^*$	206.9	0.493	0.67	4.61		0.23
	$\sigma \rightarrow \pi^*$	206.4	0.001			0.21	0.08
	$\pi \rightarrow \pi^*$	204.1	0.991	−4.85	−4.41		0.64
(B) [N]	$\sigma \rightarrow \pi^*$	335.3	0.004			0.51	0.78
	$\pi \rightarrow \pi^*$	279.9	0.079	−1.11	1.87		0.51
	$\pi \rightarrow \pi^*$	235.2	0.234		3.42		0.36
	$\sigma \rightarrow \pi^*$	203.5	0.001			−0.17	0.76
	$\pi \rightarrow \pi^*$	202.0	0.175	−1.69	2.15		0.51
	$\pi \rightarrow \pi^*$	200.1	1.167	−4.34	−5.55		0.46
	$\sigma \rightarrow \pi^*$	198.0	0.001			0.14	0.23

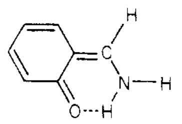
[a] The origin is at the phenyl group attachment carbon atom. [b] The number of CI states used is equal to the number of valance orbitals included. [c] Thirty-nine CI states used. [d] Forty-three CI states used. [e] (Parametrization) [structural variant].

all bond angles were assumed to be 120°.

The CNDO/S results are shown in Table III for geometry 1 and Table IV for geometry 2. In these calculations, the number of CI states used is equal to the number of valance orbitals included. The origin dependence was not investigated because of the computational time required for molecules of this large size. As can be seen in the tables, the results for parametrizations A and B are slightly different, but the trends are very similar. Geometry 2 with either parametrization gives better agreement with the experimental observation that *N*-methylbenzylidenimine (**5**) in alcohol[22] exhibits isotropic absorption (EA) maxima at 290, 245, and 205 nm[23] (Table V). This suggests that geometry 2 is a better representation of the benzylidenimine structure in agreement with the expectation that conjugation of the azomethine group with the phenyl ring will slightly shorten the phenyl–C bond and at the same time lengthen the C═N bond. With this geometry and parametrization A, the CNDO/S calculation with 39 CI states (Table IV) gives $\pi \rightarrow \pi^*$ transitions at 279.7, 248.1, and 203.4 nm in excellent agreement with the experimental results for both **5** and 17β-benzylidenimino-5α-androstan-3α-ol (**6**) (Table V). As expected, conjugation with the benzene ring now shifts the calculated $\sigma(n) \rightarrow \pi^*$ transition for the azomethine group from 311.9 nm in methylenimine (**3**) (Table II) to 337.7 nm in benzylidenimine (**4**) (Table IV). This shift is to be contrasted with the blue shift obtained by the ab initio calculation.[18] Further, the CNDO/S cal-



6, R = H
8, R = OH



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(22) The specific alcohol is not given in ref 23.

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Table IV. Results of CNDO/S Calculations Using Geometry 2

	transition						
				moment[a]			
				electric, D			magnetic, μ_B
compd[b,e]	type	wavelength, nm	oscillator strength	x	y	z	
benzylidenimine (4)[c] (A)	$\sigma(n) \rightarrow \pi^*$	337.7	0.004			0.54	0.96
	$\pi \rightarrow \pi^*$	279.7	0.001	−0.13	0.21		0.05
	$\pi \rightarrow \pi^*$	248.1	0.612	1.15	5.56		0.40
	$\sigma \rightarrow \pi^*$	206.7	<0.001			−0.06	0.27
	$\pi \rightarrow \pi^*$	203.4	0.512	4.70	−0.24		1.02
	$\sigma \rightarrow \pi^*$	198.1	<0.001			0.10	0.51
	$\pi \rightarrow \pi^*$	195.2	0.670	2.44	4.67		0.08
(B)	$\sigma(n) \rightarrow \pi^*$	322.9	0.004			0.51	0.90
	$\pi \rightarrow \pi^*$	272.7	0.007	0.49	−0.42		0.17
	$\pi \rightarrow \pi^*$	246.1	0.642	−1.24	−5.65		0.40
	$\sigma \rightarrow \pi^*$	205.4	<0.001			−0.07	0.20
	$\pi \rightarrow \pi^*$	201.3	0.508	−4.66	0.01		1.01
	$\sigma \rightarrow \pi^*$	197.1	<0.001			0.11	0.50
	$\pi \rightarrow \pi^*$	192.3	0.635	−2.01	−4.68		0.02
salicylidenimine (2)[d] (A) [O]	$\sigma \rightarrow \pi^*$	365.8	0.004			0.54	0.79
	$\pi \rightarrow \pi^*$	300.3	0.109	−0.96	2.46		0.54
	$\pi \rightarrow \pi^*$	254.1	0.246	0.05	3.64		0.37
	$\pi \rightarrow \pi^*$	213.0	0.616	−4.53	−2.71		0.69
	$\sigma \rightarrow \pi^*$	211.7	<0.001			0.16	0.82
	$\pi \rightarrow \pi^*$	209.1	0.772	2.07	5.48		0.07
	$\sigma \rightarrow \pi^*$	206.0	<0.001			0.10	0.26
(B) [O]	$\sigma \rightarrow \pi^*$	440.3	0.001			−0.32	0.18
	$\pi \rightarrow \pi^*$	337.7	0.226	−2.06	3.46		0.87
	$\pi \rightarrow \pi^*$	246.9	0.264	−1.75	−3.28		0.12
	$\sigma \rightarrow \pi^*$	246.8	<0.001			−0.03	0.64
	$\sigma \rightarrow \pi^*$	228.2	0.004			−0.43	0.50
	$\pi \rightarrow \pi^*$	226.3	0.041	−0.70	−1.22		0.03
	$\pi \rightarrow \pi^*$	213.4	0.924	3.30	5.56		0.25
(A) [N]	$\sigma \rightarrow \pi^*$	504.7	0.001			−0.34	0.18
	$\pi \rightarrow \pi^*$	356.6	0.186	−1.90	3.23		1.22
	$\sigma \rightarrow \pi^*$	273.8	<0.001			−0.02	0.67
	$\pi \rightarrow \pi^*$	255.6	0.050	−1.09	−1.23		0.26
	$\sigma \rightarrow \pi^*$	248.8	0.004			−0.45	0.50
	$\pi \rightarrow \pi^*$	233.7	0.066	−0.93	−1.55		0.04
	$\pi \rightarrow \pi^*$	220.7	1.084	3.99	5.91		0.34
(B) [N]	$\sigma \rightarrow \pi^*$	383.1	0.003			−0.50	0.64
	$\pi \rightarrow \pi^*$	294.0	0.133	−1.21	2.61		0.61
	$\pi \rightarrow \pi^*$	249.1	0.351	0.93	4.21		0.24
	$\sigma \rightarrow \pi^*$	210.5	<0.001			0.14	0.79
	$\pi \rightarrow \pi^*$	209.6	0.447	−3.99	−1.99		0.65
	$\sigma \rightarrow \pi^*$	205.8	0.001			−0.18	0.13
	$\pi \rightarrow \pi^*$	202.9	0.768	2.22	5.31		0.02

[a] The origin is at the phenyl group attachment carbon bond. [b] The number of CI states used is equal to the number of valance orbitals included. [c] Thirty-nine CI states used. [d] Forty-three CI states used. [e] (Parametrization) [structural variant].

culated electric transition moment for the π → π* transition at 248.1 nm (band II) is seen to be almost parallel to the benzene ring–methine carbon bond as suggested earlier.[1] In passing, it is to be noted that the present CNDO/S results for 4 are not identical with those obtained earlier in a similar calculation,[21] perhaps due to the different number of CI states used.

Salicylidenimine (2). The coordinate system for salicylidenimine is given in 2, the origin also chosen to be at the phenyl group attachment carbon atom. The introduction of an hydroxyl group now makes possible the formation of an intramolecular hydrogen bond (1) which complicates the matter further by the possible formation of a quinoid tautomer (7).[24] Thus, in addition to parametrizations A and B and geometries 1 and 2, another structural variant for the C–O and O–H bond distances was introduced. That with the C–O and O–H bond distances of 1.36 and 1.04 Å, respectively, is designated structural variant O, while that with a shortened C–O bond of 1.30 Å and a lengthened O–H bond of 1.35 Å to simulate the equinoid tautomer is designated structural variant N. The C–O–H bond angle was taken as 109°.

Again the CNDO/S results for different parametrizations and geometries are somewhat different, but using the same number of CI states as the number of valance orbitals included, and with parametrization A, geometry 2, and structural variant O, the calculation gives π → π* transitions at 300.3, 254.1, and 213.0 nm in excellent agreement with experimental results, typified by the EA spectrum of 17β-salicylidenimino-5α-androstan-3α-ol (8) (Table V) which shows three characteristic EA bands at 319, 258, and 217 nm in hexane designated I, II, and III, respectively. An additional EA maximum at 401 nm and a shoulder at 278 nm in the spectrum of 8 in methanol are due to the presence of the quinoid tautomer.

Similar to that found for benzylidenimine (4), the polarization of the 254.1-nm band (band II) in salicylidenimine (2) is again almost parallel to the benzene ring–methine carbon bond as deduced earlier.[1] This conforms to the observation that the Cotton effect associated with band II for the *N*-benzylidene, *N*-salicylidene, and *N*-*o*-

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(24) P. W. Alexander and R. J. Sleet, *Aust. J. Chem.*, **23**, 1183 (1970).

Table V. Spectral Data for Azomethine Derivatives

compd	solvent	band assignment	EA$_{\text{max}}$, λ, nm (ϵ^{a})	CD$_{\text{max}}$, λ, nm ($[\theta]^{b}$)
N-methylbenzylidenimine (5)^{c}	alcohol^{d}	I	290 (800)	
		II	245 (12400)	
		III	205 (21900)	
17β-benzylidenimino-5α-androstan-3α-ol (6)^{e}	hexane	I	287 (1100)	288 (−5600)
				282 (−6200)
			277 (1600)	275 (−4700)^{f}
		II	258 (14000)^{f}	
			247 (22000)	247 (+61000)
		III	211 (21000)^{f}	214 (−14000)
	MeOH			293 (+550)^{g}
		I	287 (1400)^{f}	277 (−1600)
			278 (2400)^{f}	
		II	249 (21000)	247 (+55000)
		III	212 (18000)^{f}	214 (−28000)
17β-salicylidenimino-5α-androstan-3α-ol (8)^{e}	hexane	I	319 (5100)	316 (+16000)
		$\sigma(n) \rightarrow \pi^*$		273 (−4800)
		II	263 (13000)^{f}	
			258 (15000)	253 (+25000)
		III	222 (23000)^{f}	
			217 (25000)	
	MeOH	quinoid	401 (2400)	402 (+6500)
		I	315 (3600)	315 (+13000)
		quinoid	278 (5800)^{f}	
		$\sigma(n) \rightarrow \pi^*$		275 (−3300)
		II	262 (12000)^{f}	
			257 (13000)	254 (+21000)
		III	222 (23000)^{f}	226 (−17000)
			218 (24000)	

[a] Molar absorptivity. [b] Molecular ellipticity. [c] Data from ref 23. [d] See note 22. [e] Data from ref 1. [f] Shoulder. [g] Taken to be the start of the Cotton effect centered at 247 nm.

methoxybenzylidene derivatives of a particular chiral amine all have the same sign.[1] The polarization of the 300.3-nm band, band I in **2**, although not entirely parallel to the benzene ring–methine carbon bond, has its larger component along this bond. This serves to justify the earlier assumption that the transition moments for both bands I and II of the *N*-salicylidene derivative of a chiral amine to a good approximation can be regarded as lying along the benzene ring–methine carbon bond but also serves to point to the possibility of sign differences for the Cotton effects associated with these two transitions as is infrequently observed.[7]

It is to be noted that the calculated polarizations for bands I and II in **2** agree with our previous assignments[1] which were based on the reasoning that band II is due to a charge transfer from the benzene ring to the C=N bond while band I is associated with a charge migration from the oxygen to the nitrogen atom. This agreement is somewhat puzzling since the CNDO/S calculations do not show charge transfer character for these two bands.

The 275-nm band in the CD spectrum of 17β-salicylidenimino-5α-androstan-3α-ol (**8**) in methanol (Table V) cannot be attributed to the quinoid tautomer since it persists in hexane. The band is assigned to the $\sigma(n) \rightarrow \pi^*$ transition of the azomethine group which on conjugation with the ring and intramolecular hydrogen bonding is shifted from about 245 nm in aliphatic-substituted azomethines[13,17] to about 275 nm in salicylidenimines. With parametrization A, geometry 2, and structural variant O, the CNDO/S-calculated lowest energy $\sigma \rightarrow \pi^*$ transition occurs at 365.8 nm, substantially different from 275 nm. The assignment of the 275-nm band, however, is plausible since a similar large red shift was also observed in the methylenimine CNDO/S calculation in which the 311.2-nm transition is found experimentally at about 245 nm.[13,17]

No new transition is calculated to occur at about 400 nm for structural variant N (Tables III and IV) although in one calculation a $\sigma \rightarrow \pi^*$ transition appears at 273.8 nm with the lowest energy $\sigma \rightarrow \pi^*$ transition at 504.7 nm. The poor correlation of the CNDO/S-calculated transitions with bands assigned to the quinoid tautomer in methanol indicates that structural variant N may not be a good representation of the quinoid tautomer, possibly because the bond length variation in the benzylidenimino portion of **2** was ignored.

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