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OPTICALLY ACTIVE AMINES—V[1]

COMPARISON OF THE OPTICAL ROTATORY DISPERSION AND CIRCULAR DICHROISM CURVES OF THE N-SALICYLIDENE DERIVATIVES OF SOME OPEN-CHAIN α- AND β-ARYLALKYLAMINES

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Abstract—The circular dichroism (CD) curves of the N-salicylidene derivatives of some open-chain α- and β-arylalkylamines and of α,β-diphenylethylamine in ethanol, dioxan, and isooctane were measured from 450 to about 240 mμ. In comparison with similar optical rotatory dispersion (ORD) measurements reported earlier, reliable observations to shorter wavelengths with greater resolution of the individual Cotton effects were possible. Cotton effects near 315 and 255 mμ are assigned to π–π^* transitions of the intramolecularly hydrogen-bonded salicylidenimino moiety, and for the α-arylalkylamine derivatives, an additional Cotton effect near 280 mμ is assigned to the π–π^* transition of the aromatic ring of the parent amines. The present measurements are in agreement with the conclusion drawn earlier that there is present in these derivatives an inherently dissymmetric chromophore, arising from the interaction of the π-electrons of the aryl group and the salicylidenimino moiety. However, only some of the changes in the CD curves which occur with changes in temperature could be interpreted with the simple conformational model used earlier to indicate the steric requirements for a rotationally significant interaction of the aryl and the salicylidenimino groups.

IN PREVIOUS papers[3,4] the electronic absorption spectra and ORD curves of the N-salicylidene derivatives of some α- and β-arylalkylamines (I–VII) and of α,β-diphenylethylamine (VIII) were reported.[5] With the exception of VIII, these Schiff bases in ethanol display Cotton effects near 410 and 315 mμ. With dioxan or hexane as the solvent, only the Cotton effect near 315 mμ was observed, usually enhanced in amplitude. A comparison of these curves with those of the N-salicylidene derivatives of (+)-(*S*)-sec-butylamine[5] and a number of optically active aliphatic α-amino acid esters, for which complete Cotton effects could not be observed, suggests that for the α- and β-arylalkylamine derivatives, the relatively strong Cotton effect near 315 mμ is due to an inherently dissymmetric chromophore,[6] arising from the interaction of the π-electrons of the aryl group with the salicylidenimino moiety.

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[1] Paper IV: H. E. Smith and T. C. Willis, *J. Org. Chem.* **30**, 2654 (1965).

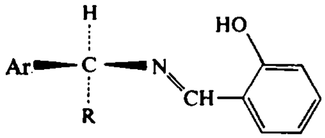
[2] To whom inquiries should be sent.

[3] H. E. Smith, S. L. Cook and M. E. Warren, Jr., *J. Org. Chem.* **29**, 2265 (1964).

[4] M. E. Warren, Jr. and H. E. Smith, *J. Amer. Chem. Soc.* **87**, 1757 (1965).

[5] For configurational assignments see Refs. 1 and 4 and footnotes and references therein. Signs in parentheses refer to rotatory powers observed with sodium D-light and with methanol or ethanol as the solvent.

[6] A. Moscowitz, *Tetrahedron* **13**, 48 (1961).



(+)-(*S*)-I, R = $C_{10}H_7$-1; R′ = CH_3
(+)-(*S*)-II, R = C_6H_5; R′ = CH_3
(−)-(*R*)-III, R = C_2H_5; R′ = C_6H_5
(−)-(*R*)-IV, R = $CH_2CO_2C_2H_5$; R′ = C_6H_5
(−)-(*R*)-V, R = $C(CH_3)_3$; R′ = C_6H_5
(+)-(*S*)-VI, R = $CH_2C_6H_5$; R′ = CH_3
(−)-L-VII, R = CO_2CH_3; R′ = $CH_2C_6H_4OH$-*p*
(−)-(*S*)-VIII, R = C_6H_5; R′ = $CH_2C_6H_5$

Considering the presence of a dissymmetric chromophore, comparison of the ORD curves of (+)-(*S*)-N-salicylidene-α-phenylethylamine (II) and (−)-(*R*)-ethyl N-salicylidene-β-aminohydrocinnamate (IV) with (−)-N-salicylidene-α-phenyl-n-propylamine (III) and (−)-N-salicylidene-α-phenylneopentylamine (V) indicates that the latter two Schiff bases have the (*R*) configuration. Similarly, the (*S*) configuration was confirmed for (+)-N-salicylidene-α-(1-naphthyl)ethylamine (I). This latter derivative was prepared from (−)-α-(1-naphthyl)ethylamine to which was assigned the (*S*) configuration on the basis of the rotatory dispersion of its N-phthaloyl derivative,[7] while the (*R*) configuration for (−)-V was subsequently established unequivocally by the stepwise conversion of (+)-α-phenylneopentylamine to (−)-D-α-benzamido-β,β-dimethylbutyric acid.[1]

We now wish to report the CD curves for these N-salicylidene derivatives and to compare these curves with those from the ORD measurements.

RESULTS

As collected in Table 1[8] and seen in Figs. 1–4, for the N-salicylidene derivatives in ethanol, the CD and ORD measurements in the 450–290 mμ region are completely parallel. With the exception of VIII, all of the derivatives with the (*S*) or D configurations show in this spectral region two positive CD maxima,[9] and thus two positive Cotton effects, one near 405 mμ and the other near 315 mμ, although for (*S*)-IV that at the longer wavelength was only observed as a positive shoulder. At wavelengths shorter than 290 mμ, the α-arylalkylamine derivatives (I–V; Figs. 1 and 2) usually display two additional maxima, a negative one near 280 mμ and a positive one near 255 mμ. Thus, for these derivatives, the unsymmetrical shape of the ORD Cotton effect near 315 mμ, with the magnitude of the molecular rotation substantially smaller for the peak than for the trough, is the result of two overlapping optically active absorption bands. For both (*S*)-IV and (*S*)-V, a negative maximum near 280 mμ was not

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[7] H. Wolf, E. Bunnenberg and C. Djerassi, *Chem. Ber.* **97**, 533 (1964).

[8] For convenience, the Schiff bases are listed in the Tables and are discussed as having the (*S*) and D configurations regardless of which isomer was actually used. Unless otherwise noted, all electronic absorption spectra and ORD and CD curves were measured at room temperature (21–28°).

[9] For CD nomenclature see, [a] C. Djerassi and E. Bunnenberg, *Proc. Chem. Soc.* 299 (1963); [b] P. Crabbé, *Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry* p. 19. Holden-Day, San Francisco (1965).

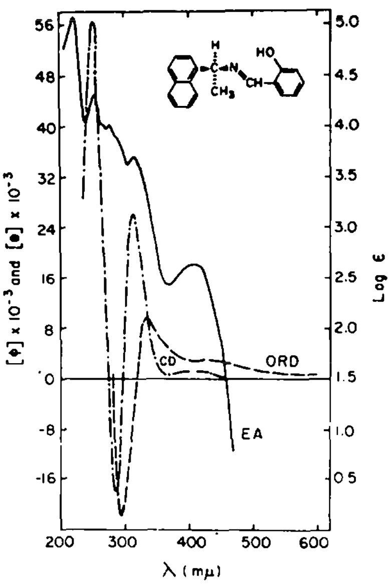


FIG. 1. (+)-(*S*)-N-Salicylidene-α-(1-naphthyl)-ethylamine (I): electronic absorption spectrum (EA) in absolute ethanol, ORD curve in 95% ethanol, and CD curve in absolute ethanol.

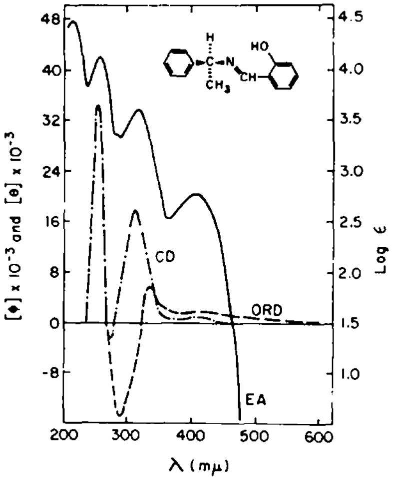


FIG. 2. (+)-(*S*)-N-Salicylidene-α-phenylethylamine (II): electronic absorption spectrum (EA) and ORD curve in 95% ethanol and CD curve in absolute ethanol.

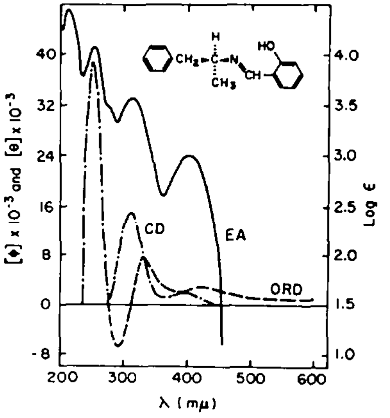


FIG. 3. (+)-(*S*)-N-Salicylidene-α-benzylethylamine (VI): electronic absorption spectrum (EA) and ORD curve in 95% ethanol and CD curve in absolute ethanol.

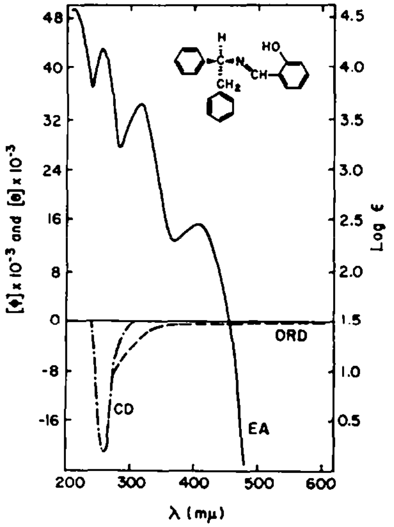
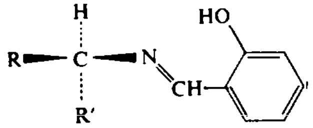


FIG. 4. (−)-(*S*)-N-Salicylidene-α,β-diphenylethylamine (VIII): electronic absorption spectrum (EA) in absolute ethanol, ORD curve in 95% ethanol, and CD curve in absolute ethanol.

TABLE 1. OPTICAL PROPERTIES OF THE N-SALICYLIDENE DERIVATIVES OF SOME OPEN-CHAIN α- AND β-ARYLALKYLAMINES IN ETHANOL



Compound substituents	Electronic absorption maxima,[c] λ, mμ (log ε)	ORD[a,b] extrema, λ, mμ ([φ][d])	CD[a,e] maxima, λ, mμ ([θ][e])
(*S*)-I	406 (2·65)	423 (+2980)	406 (+1400)
R = $C_{10}H_7$-1		405 (+2730)	
R′ = CH_3	314 (3·71)	335 (+10,000)	316 (+26,000)
		294 (−22,000)	
	290 (3·90)[f]		
	283 (4·02)		285 (−18,000)
	272 (4·03)[f]		
	256 (4·32)		256 (+57,000)
(*S*)-II	404 (2·78)[g]	428 (+1800)	405 (+1100)
R = C_6H_5		397 (+1400)	
R′ = CH_3	315 (3·61)	337 (+5900)	315 (+18,000)
		291 (−15,000)	
	283 (3·35)[f]		274 (−3000)
	256 (4·14)		253 (+34,000)
(*S*)-III[h]	405 (2·57)	428 (+2100)	402 (+1160)
R = C_6H_5		396 (+1600)	
R′ = C_2H_5	317 (3·60)	336 (+7500)	317 (+17,000)
		292 (−13,000)	
			279 (−3000)
	254 (4·12)		253 (+28,000)
(*S*)-IV[h]	404 (2·11)	430 (infl.)	415–380 (+sh.)
R = C_6H_5	317 (3·66)	337 (+8000)	322 (+16,000)
R′ = $CH_2CO_2C_2H_5$		294 (−11,000)	
	256 (4·17)		252 (+27,000)
(*S*)-V[h]	403 (2·60)	426 (+2700)	396 (+1700)
R = C_6H_5		400 (+2100)	
R′ = $C(CH_3)_3$	317 (3·61)	336 (+11,000)	314 (+19,000)
		294 (−14,000)	
	263 (4·08)[f]		
	256 (4·13)		254 (+26,000)
(*S*)-VI	402 (3·01)[g]	424 (+2900)	399 (+2000)
R = $CH_2C_6H_5$		387 (+1900)	
R′ = CH_3	315 (3·58)	333 (+7900)	312 (+15,000)
		294 (−6900)	
	280 (3·44)[f]		
	253 (4·09)		251 (+39,000)
D-VII[h]	406 (2·41)[i]	430 (infl.)[i]	415 (+940)[i]
R = $CH_2C_6H_4OH$-*p*	319 (3·58)	337 +12,000)	319 (+18,000)
R′ = CO_2CH_3		300 (−8200)	
	286 (3·46)[f]		
	256 (4·07)		262 (+44,000)
(*S*)-VIII	407 (2·45)	Plain neg.,	
R = C_6H_5	317 (3·66)	$[\phi]_{275}$ −8400°[j]	
R′ = $CH_2C_6H_5$	264 (4·12)[f]		
	258 (4·19)		262 (−21,000)

observed, but their ORD curves indicate that a negative optically active absorption band is present in this spectral region.

In contrast to these measurements, below 290 mμ the β-arylalkylamines (VI and VII; Fig. 3) displayed only one positive CD maximum, this near 255 mμ, with no indication in their ORD curves of an optically active absorption band near 280 mμ.

For the N-salicylidene derivative of (*S*)-α,β-diphenylethylamine (VIII) in ethanol (Fig. 4), only one CD maximum was observed. Contrary to the measurements using the other salicylidene derivatives (I–VII) with the (*S*) or D configuration, this Cotton effect is negative.

Summarized in Table 2 and compared graphically in Figs. 5–7 are the electronic absorption spectra and the ORD and CD curves for the N-salicylidene derivatives of (*S*)-α-phenylethylamine (II), (*S*)-α-benzylethylamine (VI), and (*S*)-α,β-diphenylethylamine (VIII) in dioxan and hexane or isooctane. As seen in Table 2 and in the Figs. 5–7 the electronic absorption maximum in ethanol near 405 mμ is changed in dioxan to a weaker shoulder centered near 410 mμ and is absent or very weak in hexane. As reported earlier for the ORD measurements in dioxan,[3,4] this shoulder was not detected as being optically active. For this same solvent, the present CD measurements are similar, and both (*S*)-II and (*S*)-VI displayed only one positive maximum, this near 315 mμ, the high dilutions necessary to penetrate the absorption bands at shorter wavelengths precluding measurements beyond about 275 mμ. As discussed elsewhere,[10] however, it is unlikely that the absorption band represented by the shoulder centered near 410 mμ is completely devoid of optical activity, but rather that its rotational strength is comparatively small and the associated Cotton effect is not usually observed. Moscowitz[11] has noted that the N-salicylidene derivative of a 20α-amino steroid in dioxan[12] displays a very feeble, positive CD maximum near 400 mμ.[13]

The observations in dioxan, where comparable, are in agreement in sign and magnitude with other CD measurements using the N-salicylidene derivatives of some 3-, 17- and 20-amino steroids[12,14] and some open-chain β-phenylalkylamines.[14] Included in this latter group are (*R*)- and (*S*)-N-salicylidene-α-benzylethylamine (VI), methyl N-salicylidene-L-phenylalaninate (IX), and (*2R,3R*)- and (*2S,3S*)-1,3-diacetoxy-1-(*p*-nitrophenyl)-2-salicylideniminopropane (X). Except for (*S*)-VI which displays positive

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[10] P. Crabbé, *Tetrahedron* **20**, 1211 (1964).

[11] Footnote 105 in Ref. 10.

[12] D. Bertin and M. Legrand, *C.R. Acad. Sci., Paris* **256**, 960 (1963).

[13] See compound IIa (Fig. 1) in Ref. 12.

[14] L. Velluz, M. Legrand and M. Grosjean, *Optical Circular Dichroism* pp. 156 and 240. Academic Press, New York, N.Y. (1965).

Footnotes to Table 1.

[a] Temp, 22–28°.

[b] 95% Ethanol as the solvent or as otherwise noted.

[c] Absolute ethanol as the solvent or as otherwise noted.

[d] Molecular rotation in degrees.

[e] Molecular ellipticity.

[f] Shoulder.

[g] 95% Ethanol as the solvent.

[h] Enantiomorph used.

[i] Methanol as the solvent.

[j] Molecular rotation at the last reliable measurement.

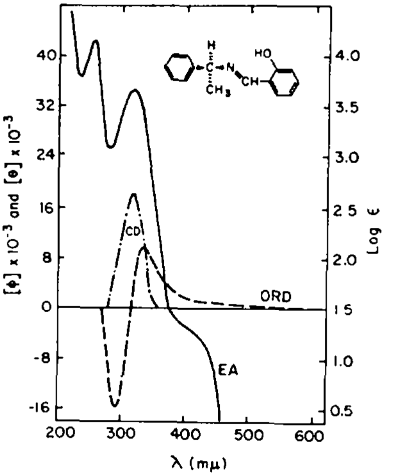


FIG. 5. (+)-(*S*)-N-Salicylidene-α-phenylethylamine (II): electronic absorption spectrum (EA) and ORD and CD curves in dioxan.

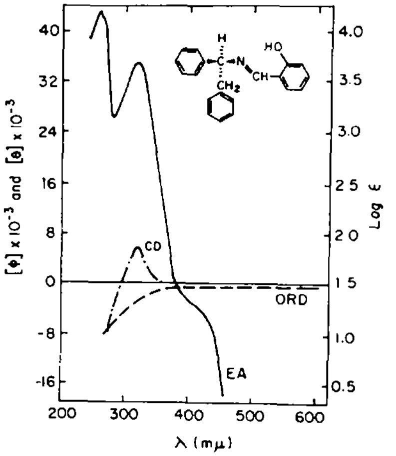


FIG. 6. (−)-(*S*)-N-Salicylidene-α,β-diphenylethylamine (VIII): electronic absorption spectrum (EA) and ORD and CD curves in dioxan.

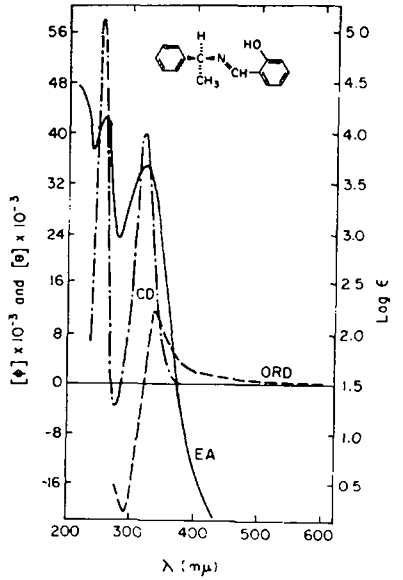


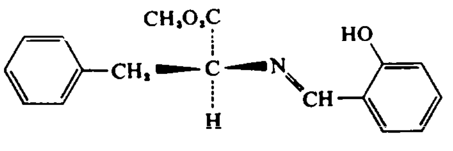
FIG. 7. (+)-(*S*)-N-Salicylidene-α-phenylethylamine (II): electronic absorption spectrum (EA) and ORD curve in hexane and CD curve in isooctane.

TABLE 2. OPTICAL PROPERTIES OF THE N-SALICYLIDENE DERIVATIVES OF SOME OPEN-CHAIN α- AND β-ARYLALKYLAMINES IN DIOXAN AND HEXANE OR ISOOCTANE

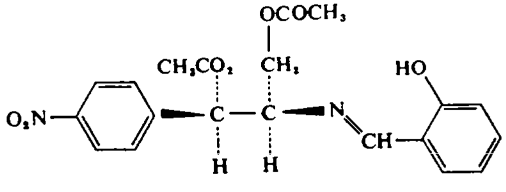
	Dioxan			Hexane		Isooctane
Compound^b	Electronic absorption maxima, λ, mμ (log ϵ)	ORD^a extrema, λ, mμ ($[\phi]^b$)	CD^a maxima, λ, mμ ($[\theta]^b$)	Electronic absorption maxima, λ, mμ (log ϵ)	ORD^a extrema, λ, mμ ($[\phi]^b$)	CD^a maxima, λ, mμ ($[\theta]^b$)
(*S*)-I	410 (1·32)^c					
	315 (3·73)	336 (+20,000)		314 (3·80)	337 (+16,000)	
		297 (−28,000)			296 (−33,000)	
	292 (3·89)^c			294 (3·94)		
				288 (3·94)		
	285 (4·01)			281 (4·05)		
	272 (4·03)^c			270 (4·07)		
	258 (4·23)			257 (4·24)		
(*S*)-II	410 (1·27)^c					
	318 (3·68)	336 (+10,000)	317 (+18,000)	320 (3·70)	336 (+12,000)	319 (+40,000)
		294 (−16,000)			290 (−21,000)	
						274 (−4000)
				262 (4·13)^c		
	257 (4·16)			255 (4·18)		253 (+58,000)
(*S*)-VI	410 (1·35)^c					
	317 (3·65)	334 (+11,000)	315 (+19,000)	318 (3·67)	336 (+14,000)	317 (+24,000)
		293 (−7000)			295 (−9000)	
	261 (4·08)^c			262 (4·10)^c		
	255 (4·13)			255 (4·15)		253 (+30,000)
(*S*)-VIII	410 (1·29)^c	Plain neg.,			Plain neg.,	
	317 (3·70)	$[\phi]_{270}$ −7700°^{e}	319 (+6000)	320 (3·72)	$[\phi]_{275}$ −7900°^{e}	
	262 (4·17)^c			263 (4·12)^c		
	257 (4·21)			257 (4·18)		258 (−15,000)

[a] Temp., 21–27°.
[b] See Table 1.
[c] Shoulder.
[d] CD not measured.
[e] Molecular rotation at the last reliable measurement.
[f] Positive Cotton effect in the 355–285 mμ region.

maxima at both 315 and 255 mμ, for all of these amino steroid and β-phenylalklamine derivatives only a maximum near 315 mμ was reported.[14] The molecular ellipticity of this maximum, negative with (*R*)-VI, L-IX and (*2R,3R*)-X and positive with (*S*)-VI and (*2S,3S*)-X, is usually greater for the β-phenylalkylamine derivatives than for the amino steroid Schiff bases. With the former group, the one exception is the easily racemized[4] α-amino acid ester derivative.



L-IX



(*2R, 3R*)-X

With (*S*)-VIII in dioxan (Fig. 6), the ORD measurements showed only a plain negative curve from 600 to 270 mμ. The CD measurements, however, reveal a weak, positive maximum at 319 mμ with a negative curve from 295 mμ to cut-off at 275 mμ.

In isooctane, the CD curves for the three derivatives examined are comparable to those in ethanol, except that a maximum near 405 mμ was not observed. For (*S*)-II in isooctane, three CD maxima are observed (Fig. 7). The negative maximum at 274 mμ reveals that for the α-arylalkylamine derivatives in hexane, as well as in ethanol, the unsymmetrical shape of the ORD Cotton effect centered near 315 mμ is due to two unresolved optically active absorption bands. In isooctane, (*S*)-VI showed only two positive maxima. For (*S*)-VIII only one negative maximum was found, the sign being the same as the ORD plain dispersion curve. The CD curve, however, does show that a positive Cotton effect occurs in the 355–285 mμ region. At 365 mμ the curve becomes positive with cut-off at 355 mμ (Experimental). At dilutions necessary to penetrate further into the absorption band with its maximum at 320 mμ, there was no recorder deflection from 355 to 285 mμ, the curve going negative at shorter wavelengths.

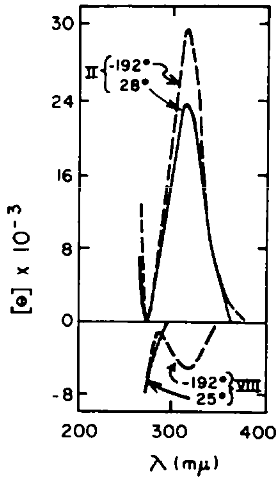


FIG. 8. (+)-(*S*)-N-Salicylidene-α-phenylethylamine (II) and (−)-(*S*)-N-salicylidene-α,β-diphenylethylamine (VIII): CD curves in EPA at 25° or 28° and −192°.

Table 3 summarizes the effect of changes in temperature on the CD curves of a number of the Schiff bases in EPA[15] using a low-temperature cell.[16] Observations were limited to wavelengths greater than about 270 mμ, and maxima were not observed at wavelengths longer than 316 mμ. As seen in the Table and in Fig. 8, with the α-phenylalkylamine derivatives (II and V), the molecular ellipticity for the maximum at 316 mμ becomes more positive by about 20% on cooling from room temperature to −192°. The rotational strength[17,18] also becomes more positive by about the same percentage. For the β-phenylalkylamine derivative (VI), comparable increases in the molecular ellipticity and rotational strength were also observed. (*S*)-N-Salicylidene-α,β-diphenylethylamine (VIII) (Fig. 8), which in EPA at 25° showed no maximum in the spectral region studied, on cooling to −192° shows a negative maximum at 314 mμ.

TABLE 3. EFFECT OF TEMPERATURE ON THE CD CURVES OF THE N-SALICYLIDENE DERIVATIVES OF SOME OPEN-CHAIN α- AND β-ARYLALKYLAMINES IN EPA[a]

Compound[b]	Temp, °C	$\lambda^{\max}$, mμ ([θ][b])	$\lambda^{\frac{1}{2}\max}$, mμ	R[c] × 10^{40}
(*S*)-II	28	316 (+24,000)	334, 295	+36
	−192	316 (+30,000)	333, 292	+48
(*S*)-V[d]	26	316 (+20,000)	335, 296	+30
	−192	316 (+23,000)	334, 295	+35
(*S*)-VI	28	315 (+20,000)	331, 297	+27
	−192	316 (+23,000)	332, 292	+36
(*S*)-VIII	25	[e]		
	−192	314 (−5300)	335, 295	−8·3

[a] Ether–isopentane–ethanol, 5:5:2 by volume.
[b] See Table 1.
[c] Rotational strength,[17,18] cgs units.
[d] Enantiomorph used.
[e] $[\theta]_{450-295}$ ±0.

DISCUSSION

For the N-salicylidene derivatives the two main absorption bands near 315 and 255 mμ have been assigned to electronic transitions of the intramolecularly hydrogen-bonded salicylidenimino group,[20] and to π–π* transitions of this group.[21] The Cotton effects appearing near these wavelengths are assigned to these excitations.

The band in ethanol and dioxan near 405 mμ has been ascribed to a tautomeric form[21] or to hydrogen-bonded complexes of the solvent with the derivative[20,22] in which the intramolecular hydrogen bond is not present.[20] Comments concerning the Cotton effect observed in this spectral region have been made earlier.[3]

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[15] Ether–isopentane–ethanol mixture in the ratio 5:5:2 by volume.

[16] K. M. Wellman, E. Bunnenberg and C. Djerassi, *J. Amer. Chem. Soc.* **85**, 1870 (1963).

[17] C. Djerassi, *Optical Rotatory Dispersion* p. 164. McGraw-Hill, New York, N.Y. (1960).

[18] Rotational strengths were calculated assuming the CD curves to be Gaussian in shape and the maximum near 316 mμ to be due to a single, isolated transition.[17] Concentration changes accompanying the volume variation with temperature were taken into consideration, but as is frequently done[19] a correction for the change in the refractive index of the solvent was ignored.

[19] See footnote 8 in A. Moscowitz, K. Wellman and C. Djerassi, *J. Amer. Chem. Soc.* **85**, 3515 (1963).

[20] J. Charette, G. Faltlhansl and Ph. Teyssie, *Spectrochim. Acta* **20**, 597 (1964).

[21] D. Heinert and A. E. Martell, *J. Amer. Chem. Soc.* **85**, 183, 188 (1963).

[22] J. Hires and L. Hackl, *Acta Univ. Szeged. Acta Phys. Chem.* **5**, 19 (1959).

For the N-salicylidene derivatives in ethanol and dioxan, an additional absorption band near 275 mμ has been associated with either the tautomeric form[21] or the solvent-bonded complex.[20] For the α-arylalkylamine derivatives, however, the negative Cotton effect present in this spectral region is most probably not associated with this absorption band since both the ORD and CD curves for these compounds in hydrocarbon solvents indicate a negative Cotton effect in this same region (Table 2). The Cotton effect is assigned rather to a π–π* transition of the aromatic ring of the parent amine, the free amines also showing absorption in the same region. For α-(1-naphthyl)-ethylamine in absolute ethanol, the absorption band, with much vibrational fine structure, has its most intense maximum at 281 mμ (log ε 3·83).[23] This same intense absorption band appears as a peak flanked by two shoulders in the absorption spectra of the N-salicylidene derivative of this amine in ethanol, dioxan, and hexane (Table 1 and 2 and Fig. 1). The parent α-phenylalkylamines of II, III and V in absolute ethanol have an absorption band with much vibrational fine structure and the most intense maximum at 257–258 mμ (log ε 2·3).[23]

The position of the negative CD maximum associated with the π–π* transition discussed above, for the α-(1-naphthyl)- and α-phenylalkylamine N-salicylidene derivatives at 285 and 276 mμ respectively, is somewhat influenced by its proximity and intensity relative to the two positive Cotton effects located at longer and shorter wavelengths.[24] Since both the positions and intensities of maxima associated with superimposed, oppositely signed Cotton effects are affected,[24] the close proximity of the three absorption bands prevented observation of the negative CD maximum for (*S*)-IV and (*S*)-V in ethanol. As seen in their ORD curves, however, there is probably a negative Cotton effect in this spectral region for both derivatives.

It is to be noted that α-benzylethylamine,[25] tyrosine[7] and probably α,β-diphenylethylamine have an absorption band centered in the 250–280 mμ region and in each N-salicylidene derivative (VI–VIII) there should be a corresponding absorption band, probably obscured by the intense absorption of the salicylidenimino group. A Cotton effect associated with this band was not detected in either the ORD or the CD curves of these derivatives.

As has been suggested earlier,[1,3,4] the large amplitude of the Cotton effect near 315 mμ in the ORD curves of the N-salicylidene derivatives of the α- and β-arylalkylamines (I–VII) and now the high molecular ellipticities of the positive CD maxima near 315 and 255 mμ indicate that there is present in the intramolecularly hydrogen-bonded species an inherently dissymmetric chromophore. Both (*S*)-II and (*S*)-V display strong positive Cotton effects, even though, due to a difference in the effective bulk size of the alkyl group attached to the asymmetric center, each Schiff base has a different preferred conformation.[1] Thus, regardless of the size of the alkyl group, the N-salicylidene of an α-arylalkylamine with the structure and configuration XI (Ar = C_6H_5 or $C_{10}H_7$-1; R = alkyl group) will, without the intervention of certain other factors,[1] display positive Cotton effects near 315 and 255 mμ. For the enantiomorph, the Cotton effects will be negative. It appears also that this generalization applies to

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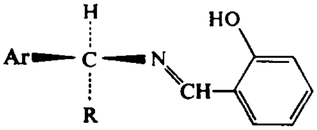
[25] *Organic Electronic Spectral Data* (Edited by M. J. Kamlet) Vol. 1; p. 279. Interscience, New York N.Y. (1960).



XI

the N-salicylidene derivatives of certain β-phenylalkylamine derivatives (Ar = $CH_2C_6H_5$ in XI), a contiguous asymmetric center, such as that in X, having only an insignificant effect.

The CD measurements for the derivatives in EPA, however, do not augment the argument for this suggestion, and for both (*S*)-II and (*S*)-V, the rotational strength of the Cotton effect near 315 mμ is increased on cooling. The difficulty here probably resides in the extremely large range of possible conformers for these derivatives and detailed considerations become difficult. Work with conformationally more rigid derivatives may indicate more exactly the steric requirements for rotationally significant interactions of the phenyl, 1-naphthyl and benzyl groups with the salicylidenimino moiety.

The CD measurements with (*S*)-N-salicylidene-α,β-diphenylethylamine (VIII) are of special interest. In ethanol only a negative CD maximum at 262 mμ was observed. In dioxan an additional positive maximum at 319 mμ was found. A negative maximum near 262 mμ could not be observed, but below 295 mμ the curve is negative to cut-off at 275 mμ. In addition, the ORD curve in dioxan, very similar to that in ethanol, indicated that in dioxan the absorption band at 257 mμ gives rise to a negative Cotton effect. With the CD measurements in isooctane, both a positive and a negative Cotton effect were detected, although for the positive one at the longer wavelength, observations were not possible through the complete maximum.

These data are interpreted as reflecting for each Cotton effect the algebraic sum of the rotatory contributions of the intramolecularly hydrogen-bonded conformers of (*S*)-VIII.[1] In ethanol, dioxan and isooctane, the shorter wavelength Cotton effect near 260 mμ is negative, and in the latter two solvents the other near 319 mμ is positive. In EPA at room temperature, the longer wavelength Cotton effect was not detected. On cooling to −192°, however, the conformational equilibrium is shifted toward the conformer of lowest energy, and a negative maximum at 314 mμ is observed.

EXPERIMENTAL

Circular dichroism measurements. CD measurements were made using a Baird-Atomic/Jouan dichrograph operating with a photomultiplier voltage of 1·1 kv increased frequently to 1·3 kv in regions of high absorption, concentrations such that the slit width was no greater than 1·4 mm at the CD maxima or as otherwise noted, and an instrument sensitivity setting of 1·5. The cell path length was 0·2 dm. Molecular ellipticity, $[\theta]$, was calculated as $[\theta] = 2{\cdot}303(4500/\pi)(\epsilon_L - \epsilon_R)$ with $(\epsilon_L - \epsilon_R) = d \times \text{sensitivity} \times 10^{-6} \times \text{mol wt}/c \times l$, where *d* is the recorder deflection in mm, *c* is the concentration in g/100 ml and *l* is the cell path length in dm.

CD curves are reported by recording for each concentration used, $[\theta]$ at 450 mμ or at the wavelength at which cut-off occurred at the next higher concentration, at the shortest wavelength before cut-off, and at each maximum and minimum, and by indicating the wavelengths at which $[\theta]$ was zero or over which it was constant.

(+)-(S)-N-*Salicylidene*-α-(1-*naphthyl*)*ethylamine* (I), $[\alpha]_D^{24}$ +311° (*c* 2·0, abs EtOH); CD (Fig. 1) in abs EtOH, 27°: (*c* 0·041) $[\theta]_{450}$ +370, $[\theta]_{406}$ +1400, $[\theta]_{369}$ +730, $[\theta]_{352}$ +1700; (*c* 0·0081) $[\theta]_{352}$ +1400, $[\theta]_{340}$ +6400; (*c* 0·0032) $[\theta]_{340}$ +5000, $[\theta]_{316}$ +26,000, $[\theta]_{300}$ +13,000; (*c* 0·0016) $[\theta]_{300}$ +11,000, $[\theta]_{297}$ ±0, $[\theta]_{285}$ −18,000, $[\theta]_{275}$ ±0; (*c* 0·00065) $[\theta]_{275}$ ±0, $[\theta]_{256}$ +57,000, $[\theta]_{237}$ +29,000.

(+)-(S)-N-*Salicylidene-α-phenylethylamine* (II), $[\alpha]_D^{25}$ +188° (*c* 1·2, MeOH); CD (Fig. 2) in abs EtOH, 25–28°: (*c* 0·049) $[\theta]_{450}$ +190, $[\theta]_{405}$ +1100, $[\theta]_{366}$ +750, $[\theta]_{360}$ +880; (*c* 0·0098) $[\theta]_{360}$ +600, $[\theta]_{340}$ +4400; (*c* 0·0039) $[\theta]_{340}$ +5000, $[\theta]_{315}$ +18,000, $[\theta]_{280}$ ±0, $[\theta]_{274}$ −3000, $[\theta]_{267}$ ±0; (*c* 0·00090) $[\theta]_{267}$ ±0, $[\theta]_{253}$ +34,000, $[\theta]_{235}$ ±0; CD (Fig. 5) in dioxan, 27°: (*c* 0·10) $[\theta]_{450}$ ±0, $[\theta]_{385}$ ±0, $[\theta]_{360}$ +380; (*c* 0·010) $[\theta]_{360}$ ±0, $[\theta]_{345}$ +2900; (*c* 0·0042) $[\theta]_{345}$ +2900, $[\theta]_{330}$ +13,000; (*c* 0·0021) $[\theta]_{330}$ +15,000, $[\theta]_{317}$ +18,000, $[\theta]_{280}$ ±0, $[\theta]_{270}$ ±0; (*c* 0·00083) no observable recorder deflection, 270–266 mμ; (*c* 0·00042) no observable recorder deflection, 266–254 mμ; CD (Fig. 7) in isooctane, 25°: (*c* 0·053) $[\theta]_{450}$ ±0, $[\theta]_{380}$ ±0, $[\theta]_{365}$ +690; (*c* 0·011) $[\theta]_{365}$ +900, $[\theta]_{355}$ +3500; (*c* 0·0053) $[\theta]_{355}$ +2900, $[\theta]_{345}$ +7500; (*c* 0·0021) $[\theta]_{345}$ +9000, $[\theta]_{335}$ +22,000; (*c* 0·0011) $[\theta]_{335}$ +23,000, $[\theta]_{319}$ +40,000 (slit 2·0 mm), $[\theta]_{295}$ +9,000; (*c* 0·0021) $[\theta]_{295}$ +13,000, $[\theta]_{284}$ ±0, $[\theta]_{274}$ −4000, $[\theta]_{268}$ ±0; (*c* 0·00053) $[\theta]_{268}$ ±0, $[\theta]_{260}$ +23,000; (*c* 0·00042) $[\theta]_{260}$ +22,000, $[\theta]_{253}$ +58,000, $[\theta]_{235}$ +7000; CD (Fig. 8) in EPA, 28°: (*c* 0·0047) $[\theta]_{450}$ ±0, $[\theta]_{360}$ ±0, $[\theta]_{316}$ +24,000, $[\theta]_{275}$ ±0, $[\theta]_{269}$ +7000; CD (Fig. 8) in EPA, −192°: (*c* 0·0058[26]) $[\theta]_{450}$ ±0, $[\theta]_{380}$ ±0, $[\theta]_{316}$ +30,000, $[\theta]_{272}$ ±0, $[\theta]_{267}$ +13,000.

(−)-(R)-N-*Salicylidene-α-phenyl*-n-*propylamine* (III), $[\alpha]_D^{24}$ −161° (*c* 2·0, abs EtOH); CD in abs EtOH, 27°: (*c* 0·050) $[\theta]_{450}$ −130, $[\theta]_{402}$ −1160, $[\theta]_{371}$ −770, $[\theta]_{360}$ −900; (*c* 0·010) $[\theta]_{360}$ −700, $[\theta]_{350}$ −1600; (*c* 0·0040) $[\theta]_{350}$ −1600, $[\theta]_{317}$ −17,000, $[\theta]_{282}$ ±0, $[\theta]_{279}$ +3000, $[\theta]_{268}$ ±0; (*c* 0·00080) $[\theta]_{268}$ ±0, $[\theta]_{253}$ −28,000, $[\theta]_{239}$ ±0, $[\theta]_{236}$ ±0.

(−)-(R)-*Ethyl* N-*salicylidene-β-aminohydrocinnamate* (IV), $[\alpha]_D^{24}$ −84·3° (*c* 1·5, abs EtOH); CD in abs EtOH, 26°: (*c* 0·11) $[\theta]_{450}$ ±0, $[\theta]_{415}$ −220, $[\theta]_{380}$ −220, $[\theta]_{355}$ −330; (*c* 0·011) $[\theta]_{355}$ −400, $[\theta]_{340}$ −4400; (*c* 0·0044) $[\theta]_{340}$ −6000, $[\theta]_{322}$ −16,000, $[\theta]_{287}$ ±0; (*c* 0·00088) $[\theta]_{287}$ ±0, $[\theta]_{270}$ ±0, $[\theta]_{252}$ −27,000, $[\theta]_{237}$ ±0.

(−)-(R)-N-*Salicylidene-α-phenylneopentylamine* (V), $[\alpha]_D^{20}$ −251° (*c* 0·99, MeOH); CD in abs EtOH, 25°: (*c* 0·065) $[\theta]_{450}$ −220, $[\theta]_{420}$ −660; (*c* 0·013) $[\theta]_{420}$ −800, $[\theta]_{396}$ −1700, $[\theta]_{374}$ −800, $[\theta]_{350}$ −2500; (*c* 0·0026) $[\theta]_{350}$ −3000, $[\theta]_{314}$ −19,000, $[\theta]_{270}$ ±0; (*c* 0·0012) $[\theta]_{270}$ ±0, $[\theta]_{254}$ −26,000, $[\theta]_{239}$ ±0; CD in EPA, 26°: (*c* 0·0056) $[\theta]_{450}$ ±0, $[\theta]_{347}$ ±0, $[\theta]_{316}$ −20,000, $[\theta]_{277}$ ±0, $[\theta]_{268}$ ±0; CD in EPA, −192°: (*c* 0·0070[26]) $[\theta]_{450}$ ±0, $[\theta]_{354}$ ±0, $[\theta]_{316}$ −23,000, $[\theta]_{269}$ ±0.

(+)-(S)-N-*Salicylidene-α-benzylethylamine* (VI), $[\alpha]_D^{24}$ +346° (*c* 1·0, abs EtOH); CD (Fig. 3) in abs EtOH, 25–28°: (*c* 0·029) $[\theta]_{450}$ ±0, $[\theta]_{399}$ +2000, $[\theta]_{382}$ +1200, $[\theta]_{355}$ +1400; (*c* 0·012) $[\theta]_{355}$ +1500, $[\theta]_{340}$ +4000; (*c* 0·0058) $[\theta]_{340}$ +4900, $[\theta]_{330}$ +9200; (*c* 0·0023) $[\theta]_{330}$ +8000, $[\theta]_{312}$ +15,000, $[\theta]_{278}$ +1000, $[\theta]_{270}$ +5000; (*c* 0·00092) $[\theta]_{270}$ +7000, $[\theta]_{251}$ +39,000, $[\theta]_{225}$ ±0; CD in dioxan, 25°: (*c* 0·056) $[\theta]_{450}$ ±0, $[\theta]_{385}$ ±0, $[\theta]_{355}$ +580; (*c* 0·011) $[\theta]_{355}$ +600, $[\theta]_{345}$ +2600; (*c* 0·0022) $[\theta]_{345}$ +3000, $[\theta]_{315}$ +19,000, $[\theta]_{275}$ +1000; (*c* 0·0011) no observable recorder deflection, 275–240 mμ; CD in isooctane, 25°: (*c* 0·065) $[\theta]_{450}$ ±0, $[\theta]_{400}$ ±0, $[\theta]_{350}$ +840; (*c* 0·013) $[\theta]_{350}$ +740, $[\theta]_{345}$ +2500; (*c* 0·0026) $[\theta]_{345}$ +2500, $[\theta]_{317}$ +24,000, $[\theta]_{275}$ +1200; (*c* 0·00065) $[\theta]_{275}$ ±0, $[\theta]_{252}$ +30,000, $[\theta]_{238}$ ±0; CD in EPA, 28°: (*c* 0·082) $[\theta]_{450}$ ±0, $[\theta]_{380}$ ±0, $[\theta]_{347}$ +890; (*c* 0·0082) $[\theta]_{347}$ +800, $[\theta]_{340}$ +4900; (*c* 0·0033) $[\theta]_{340}$ +4000, $[\theta]_{315}$ +20,000, $[\theta]_{270}$ ±0; CD in EPA, −192°: (*c* 0·0041[26]) $[\theta]_{380}$ ±0, $[\theta]_{360}$ ±0, $[\theta]_{316}$ +23,000, $[\theta]_{275}$ ±0.

(−)-*Methyl* N-*salicylidene*-L-*tyrosinate* (VII), $[\alpha]_D^{22}$ −270° (*c* 2·0, MeOH); CD in MeOH, 26°: (*c* 0·0051) $[\theta]_{450}$ −80, $[\theta]_{418}$ −940, $[\theta]_{410}$ −860, $[\theta]_{380}$ −860; (*c* 0·0010) $[\theta]_{350}$ −700, $[\theta]_{345}$ −6000; (*c* 0·00041) $[\theta]_{345}$ −7000, $[\theta]_{319}$ −18,000, $[\theta]_{290}$ −2000; (*c* 0·000082) $[\theta]_{290}$ ±0, $[\theta]_{262}$ −44,000, $[\theta]_{244}$ −15,000.

(−)-(S)-N-*Salicylidene-α,β-diphenylethylamine* (VIII), $[\alpha]_D^{23}$ −89° (*c* 0·88, abs EtOH); CD (Fig. 4) in abs EtOH, 25–26°: (*c* 0·0050) $[\theta]_{450}$ ±0, $[\theta]_{305}$ ±0, $[\theta]_{285}$ −3300; (*c* 0·0010) $[\theta]_{285}$ −4000, $[\theta]_{262}$ −21,000, $[\theta]_{240}$ ±0, $[\theta]_{235}$ ±0; CD in dioxan, 25°: (*c* 0·068) $[\theta]_{450}$ ±0, $[\theta]_{370}$ ±0, $[\theta]_{350}$ +420; (*c* 0·0068) $[\theta]_{350}$ +600, $[\theta]_{319}$ +6000 (slit 2·0 mm), $[\theta]_{295}$ ±0, $[\theta]_{290}$ −1200; (*c* 0·0034) $[\theta]_{290}$ −1200, $[\theta]_{275}$ −7200; (*c* 0·00085) no observable recorder deflection, 275–240 mμ; CD in isooctane, 25°: (*c* 0·067) $[\theta]_{450}$ ±0, $[\theta]_{365}$ ±0, $[\theta]_{355}$ +240; (*c* 0·0067) $[\theta]_{358}$ ±0, $[\theta]_{340}$ ±0; (*c* 0·013) $[\theta]_{340}$ ±0, $[\theta]_{285}$ ±0, $[\theta]_{255}$ −15,000, $[\theta]_{241}$ ±0; CD (Fig. 8) in EPA, 25°: (*c* 0·0076) $[\theta]_{450}$ ±0, $[\theta]_{295}$ ±0, $[\theta]_{270}$ −8000; CD (Fig. 8) in EPA, −192°: (*c* 0·0095[26]) $[\theta]_{450}$ ±0, $[\theta]_{350}$ ±0, $[\theta]_{314}$ −5300, $[\theta]_{288}$ −900, $[\theta]_{270}$ −7900.

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[26] On cooling, a concentration correction factor of 1·253 was applied.