Optically Active Amines. 28.[1] Spectral Observations on Chiral N-Substituted *p*-Nitroanilines[2]

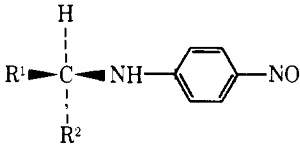
Howard E. Smith,*[3a] William I. Cozart,[3a] Tomas de Paulis,[3a] and Fu-Ming Chen[3b]

Contribution from the Departments of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, and Tennessee State University, Nashville, Tennessee 37203. *Received August 25, 1978*

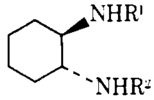
Abstract: Electronic absorption (EA) and circular dichroism (CD) measurements with a series of chiral N-substituted *p*-nitroanilines in conjunction with CNDO/S calculations with *p*-nitroaniline show that the strong absorption band of *p*-nitroaniline in polar solvents at about 385 nm is long (*z*) axis polarized and that near 235 nm contains a strong short (*x*) axis and a weak *z* axis polarized transition. These are assigned as transitions to the $2A_1$, $3B_1$, and $3A_1$ and/or $4A_1$ excited states, respectively. The weak shoulders at about 315, 300, and 265 nm are identified as *x* axis polarized. The low-energy pair is assigned to totally symmetric vibrational modes of the $1B_1$ transition, and the other to the $2B_1$ transition. These assignments are, with minor exceptions, in general agreement with those made previously.

Electronic absorption (EA) spectral studies of *p*-nitroanilines are important since the *p*-nitroaniline chromophore is an outstanding example of a polar organic group incorporating both strong electron-donor and electron-acceptor moieties for which electron-transfer bands are expected to be prominent. Indeed, the EA spectrum of *p*-nitroaniline has been extensively studied,[4-10] but some of the absorption band assignments were still unclear. The EA spectrum of the *p*-nitroaniline chromophore is typified by that of (*R*)-*N*-(1,2,2-trimethylpropyl)-*p*-nitroaniline [(*R*)-**1**] in methanol (Figure 1 and Table I) which exhibits an intense long wavelength band at 392 nm (ϵ_{max} 22 000) and a broad moderate band at 234 nm (ϵ_{max} 7900) with shoulders at 315, 300, and 265 nm. These transitions have been variously assigned based on electric dichroic,[5] single crystal,[4,9] stretched film dichroic,[6] and magnetic circular dichroic[8] absorption measurements as well as molecular orbital calculations.[7,9,10] The location of the intense long-wavelength band is very solvent dependent and has been observed at 364–370 nm in single crystals,[4,9] at 385 nm in polar solvents,[7] and at 323 nm in nonpolar solvents.[7] The assignment of this transition as long axis (*z*) polarized with strong charge-transfer character has been generally accepted. The 234-nm band is believed to be in-plane short axis (*x*) polarized with partial contribution from a weak z-polarized transition at about 222 nm.[7,8,10] There is, however, some disagreement as to the assignment of the transition in the 300-nm region. An additional intense absorption band at about 190 nm has also been observed by Khalil and McGlynn[7] who extended their measurements below 200 nm. Based on comparison with their CNDO/S calculation, this band was assigned to be *z*-polarized.[7,10]

The useful feature of circular dichroism (CD) measurements in assisting in the location and assignment of electronic transitions[11,12] has prompted us to measure the EA and CD spectra of a number of chiral N-substituted *p*-nitroanilines (**1–7**). These derivatives were prepared by condensation of *p*-fluoronitrobenzene with the corresponding chiral amine,[13] (*R*)-**7** being prepared in two steps by way of (*R*)-**8**. The amines, except for that corresponding to (*S*)-**5**, were characterized in connection with other work.[14-18] Application of the salicylidenimino chirality rule[18] to an interpretation of the CD spectrum of the *N*-salicylidene derivative of the latter amine now confirms its previously assigned configuration.[19]



(*R*)-**1**, $R^1 = CH_3$; $R^2 = C(CH_3)_3$
(*S*)-**2**, $R^1 = C_6H_5$; $R^2 = CH_3$
(*R*)-**3**, $R^1 = C(CH_3)_3$; $R^2 = C_6H_5$
(*S*)-**4**, $R^1 = 1\text{-}C_{10}H_7$; $R^2 = CH_3$
(*S*)-**5**, $R^1 = 2\text{-}C_4H_3O$; $R^2 = CH_3$
(*R*)-**6**, $R^1 = CH_3$; $R^2 = 2\text{-}C_4H_3S$



(*R*)-**7**, $R^1 = R^2 = C_6H_4NO_2\text{-}p$
(*R*)-**8**, $R^1 = C_6H_4NO_2\text{-}p$; $R^2 = H$

The EA and CD spectra of the *p*-nitroaniline derivatives are summarized in Tables I and II, shown in the figures, and discussed for the enantiomers with the *R* configuration regardless of the enantiomer actually used.

Results and Discussion

(*R*)-*N*-(1,2,2-Trimethylpropyl)-*p*-nitroaniline [(*R*)-1]. Complementary to the EA spectrum of (*R*)-**1** in methanol, its CD spectrum (Figure 1) clearly shows positive maxima at 316, 304, 258, and 212 nm and a negative maximum at 227 nm. The Cotton effect associated with the 392-nm absorption band could not be observed in our instrument (Cary Model 60 with a CD Model 6001 accessory) because of a very unfavorable anisotropy factor ($\Delta\epsilon/\epsilon$) but is easily inferred to be negative from the rotatory power of (*R*)-**1** at the sodium D line (Table IV) as well as CD measurements in ether–isopentane–ethanol (EPA) using another instrument (JASCO Model J-40A) (Figure 2).

The usefulness of CD measurements in detecting weak transitions is clearly demonstrated by the appearance in the CD spectrum of (*R*)-**1** in methanol of apparent maxima at 316, 304, and 258 nm in contrast to mere shoulders at about these same wavelengths in the EA spectrum. That the signs of the CD bands give information on the relative orientation of the respective transition moments is especially true for the *p*-nitroaniline chromophore which can be approximated as having C_{2v} symmetry. As a result, its electric transition moments can only be either along or perpendicular to its long axis. Although transitions of different polarization do not necessarily have different CD signs, the appearance of oppositely signed CD bands does signify different polarizations if the mechanism for the generation of the Cotton effects is the same. Consequently, the observation that the 315-, 300-, and 265-nm EA bands exhibit Cotton effects with sign different from that of the 392-nm band, which is known to be *z*-polarized (A_1 symmetry), implies that the former transitions are *x*-polarized (B_1 symmetry). Furthermore, the appearance of oppositely signed Cotton effects near 234 nm indicates the existence of two or more transitions of different polarization in this spectral region in agreement with previous assignments.[7,8,10]

0002-7863/79/1501-5186$01.00/0

Table I. Spectral Data for Chiral N-Substituted *p*-Nitroanilines in Methanol

		CD[a]		
compd	EA max λ, nm (ε[c])	max λ, nm ([θ][b])	min λ, nm ([θ][b])	[θ][b] = ±0 λ, nm[d]
(*R*)-**1**	392 (22 000)	(−)[e]		320
	315 (1600)[f]	316 (+1100)	310 (±0)	
	300 (1200)[f]	304 (+300)	295 (±0)	
	265 (1800)[f]	258 (+1200)		240
	234 (7900)			
		227 (−2400)		223
		212 (+4100)		208
(*R*)-**2**[g]				435
	384 (20 000)	387 (+4900)	380 (+4400)	
		374 (+5500)	319 (+700)	
	310 (2000)[f]	309 (+3100)	305 (+2800)	
	297 (1500)[f]	300 (+3200)		273
		270 (−1500)		268
		267 (+600)		265
		263 (−400)		262
	257 (2700)[f]	258 (+2200)[f]		
		245 (+6100)		235[h]
	230 (8400)			
(*R*)-**3**				443
	386 (21 000)	388 (+9500)[i]	323 (+580)	
		308 (+6100)	304 (+5100)	
	298 (1000)[f]	300 (+6100)		
		275 (+600)[f]	270 (+300)	
		266 (+2400)[f]		
	260 (3000)[f]	258 (+5800)[f]		
		246 (+11 000)		232
	229 (9000)	226 (−5700)		221
(*R*)-**4**[g]				450
	384 (20 000)	375 (−10,000)[i]		316
	308 (2500)[f]	310 (+8100)	306 (+6100)	
		304 (+6400)		300
	290 (6100)[f]	293 (−18 000)[f]		
		288 (−19 000)[f]		
		284 (−21 000)		
	282 (7700)	282 (−19 000)[f]	264 (−9700)	
	272 (7000)			
	263 (5900)[f]			
	223 (84 000)	227 (−410 000)		217
(*R*)-**5**[g]				445
	380 (17,000)	380 (+5400)[i]	318 (+1100)	
		308 (+1900)	303 (+900)	
	298 (2100)[f]	297 (+1600)	275 (+300)	
		235 (+18 000)		222
	213 (14,000)[f]			
(*R*)-**6**				450
	382 (19 000)	380 (+7700)[i]	320 (+1200)	
	310 (2200)[f]	308 (+4900)	303 (+4600)	
	298 (1600)[f]	298 (+5000)	279 (+1000)	
		253 (+15 000)		238
	233 (15 000)			
(*R*)-**7**				475
		414 (+200 000)		
	392 (48 000)			388
		368 (−140 000)		
	314 (4300)[f]			
	303 (3100)[f]			300
		287 (+2000)[f]		
		266 (+6900)		
				250
		244 (−4600)		
	231 (19 000)			
		225 (+14 000)[f,i]		206[j]

---

[a] Temperature 25-28 °C; *c* 1.09×10^{-5} to 3.43×10^{-2} g/100 mL, length 1 cm. [b] Molecular ellipticity. [c] Molar absorptivity. [d] Each first entry indicates the interval from the longest wavelength examined (600 nm) for which [θ] = ±0, and each last entry is cut-off. [e] Deduced on the basis of the rotatory power at D line and the CD measurement in EPA at 25 and −196 °C. [f] Shoulder. [g] Enantiomer used. [h] [θ] = +2600. [i] Very broad. [j] [θ] = +110 000.

Table II. Circular Dichroism Data for Chiral N-Substituted *p*-Nitroanilines in EPA[a]

	25 °C			−196 °C		
compd	max λ, nm ([θ][b])	min λ, nm ([θ][b])	[θ][b] = ±0 λ, nm[c]	max λ, nm ([θ][b])	min λ, nm ([θ][b])	[θ][b] = ±0 λ, nm[c]
(*R*)-**1**			422			425
	376 (−3400)		320	412 (−3100)	406 (−2000)	
	314 (+1300)		309	402 (−4100)	397 (−900)	
				390 (−3300)		345
						325
				312 (+6600)	308 (+3800)	
				303 (+5200)	285 (+3100)	
				280 (+3600)	276 (+2800)	
				270 (+3100)	260 (+2700)	
				256 (+3300)	253 (+1900)	
				246 (+6000)	243 (+3100)	
				239 (+5200)		235[d]
(*R*)-**2**[e]			458			470
	382 (+5000)	368 (+4600)		404 (+9500)	399 (+8300)	
	360 (+4800)	318 (+1700)		390 (+8800)	318 (+800)	
	306 (+5000)	302 (+4300)		308 (+7000)	305 (+3000)	
	297 (+5000)			299 (+5000)		
	275 (+2200)[f]	268 (±0)		291 (+3300)[f]		
	265 (+1700)	262 (+700)		282 (+1600)[f]		278
	248 (+5000)		240	271 (−4200)[f]		
				268 (−8300)	265 (−3700)	
				261 (−7000)	257 (−2100)	
				256 (−3600)		
				253 (−1500)[f]		250[g]
(*R*)-**3**			425			424
	372 (+9600)	318 (+700)		402 (+19 000)[f]		
	307 (+8300)	303 (+6700)		391 (+27 000)		334
	297 (+7800)		272			322
	269 (−1300)		267	309 (+17 000)	305 (+6100)	
	265 (+1500)	263 (+1100)		300 (+13 000)	294 (+5300)	
	257 (+6300)[f]			290 (+6700)		277
	252 (+8500)		240	276 (−2000)		274
	232 (−7300)		225	272 (+1400)		271
				270 (−1000)		268
				264 (+5600)[f]		
				259 (+8700)	256 (+8100)	
				249 (+11 000)		234

[a] *c* 1.06–2.04 mg/100 mL in ether-isopentane-ethanol, 5:5:2 by volume; length 1 cm. [b] Molecular ellipticity. [c] Each first entry indicates the interval from the longest wavelength examined (470 nm) for which [θ] = ±0, and each last entry is cut-off. [d] [θ] = +3800. [e] Enantiomer used. [f] Shoulder. [g] [θ] = −400.

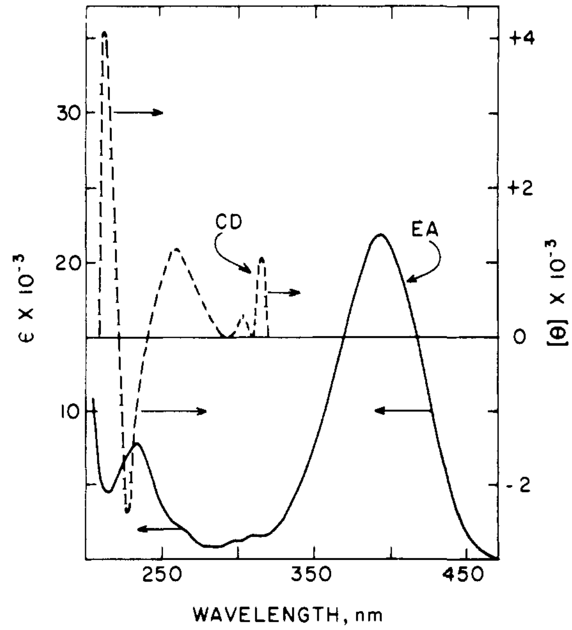


Figure 1. Electronic absorption (EA) and circular dichroism (CD) spectra of (*R*)-*N*-(1,2,2-trimethylpropyl)-*p*-nitroaniline [(*R*)-**1**] in methanol.

The CD spectra of (*R*)-**1** in EPA at 25 and −192 °C are summarized in Table II and shown in Figure 2. The obvious difference between the two spectra is the appearance of fine structure and an increase in rotational strength at the lower temperature. It should be noted, however, that the rotational strength increase is more pronounced for the 314-nm band than for the 392-nm band as is expected since rotational averaging as the temperature increases will be more effective for transitions with short axis polarization. The great clarity of vibrational fine structure in the low-temperature spectrum in the 303- to 312-nm region enables the assignment of the 312- and 303-nm maxima to be members of the totally symmetric vibrational progression of 950 cm^{-1} of the B_1 transition and the minima starting at 308 nm, 400 cm^{-1} from the band origin, to belong to the nontotally symmetric vibrational progression of this same transition. It is to be noted that this nontotally symmetric vibronic progression is *z*-polarized. The symmetric vibration may be due to the symmetric stretch of the carbon-nitro group bond and/or the symmetric deformation of the phenyl ring of about 840 cm^{-1},[20] and the nontotally symmetric vibration may be that of the nitro group asymmetric deformation of about 535 cm^{-1}.[20]

(*R*)-*trans*-*N*,*N*′-Di(*p*-nitrophenyl)-1,2-cyclohexyldiamine [(*R*)-7]. The intense long-wavelength transition of the *p*-nitroaniline chromophore has been generally accepted as *z*-

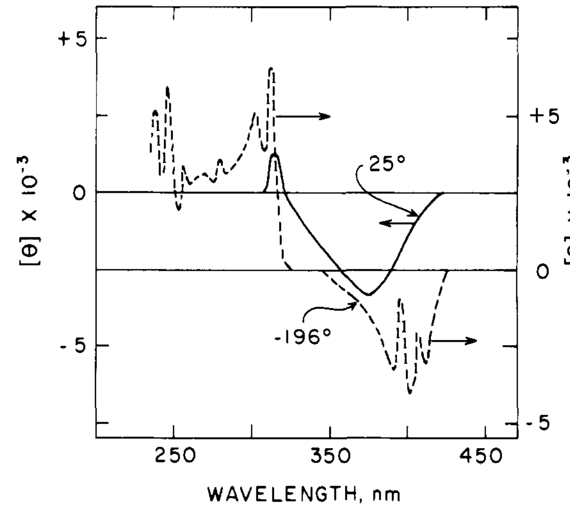


Figure 2. Circular dichroism spectra of (R)-N-(1,2,2-trimethylpropyl)-p-nitroaniline [(R)-**1**] in EPA at 25 and −196 °C.

polarized, and the CD of (R)-**7** is in agreement with this assignment. According to exciton theory,[18,21] the dipolar interaction between two identical transition moments, μ_1 and μ_2, will split the excited states into two, A and B, with energies $E(\mathrm{A}) = E_0 + V_{12}$ and $E(\mathrm{B}) = E_0 - V_{12}$, where E_0 is the energy state of a single group. The corresponding rotational strengths are given by

$$R\begin{pmatrix}\mathrm{A}\\ \mathrm{B}\end{pmatrix} = \mp\left(\frac{\pi}{2\lambda_0}\right)\mathbf{R}_{12}\cdot\mu_1 \times \mu_2$$

where $\mathbf{R}_{12}$ is a vector directing from transition 1 to transition 2 and λ_0 is the transition wavelength. When a molecule has C_2 symmetry, A and B represent the in-phase and out-of-phase coupling modes, respectively. Consequently, if the dipolar interaction energy is positive, the long-wavelength band of the exciton couplet will always be B mode and will be positive for positive chirality and negative otherwise. This statement is also applicable to an exciton couplet between two different transition moments. Thus, the pattern of exciton splitting can give information concerning the transition moment direction.

The CD spectrum of (R)-**7** (Table I) in methanol clearly shows exciton splitting centered near 390 nm. The exciton splitting indicates that the transition moment directions are not rotationally averaged to any great extent in agreement with the long axis (z) polarization of the p-nitroaniline chromophore. Since the exciton interaction is directly related to the relative orientation of the two interacting transition moments, a rotationally averaged transition moment will be doubly ineffective in exciton splitting. Indeed the short axis (x) polarized transition moments do not exhibit exciton splitting in the CD spectrum of (R)-**7**. Thus the exciton splitting observed at 250 nm also indicates the presence of a z-polarized transition in this spectral region. The intense positive CD absorption at cut-off (206 nm) can be regarded as the beginning of the long-wavelength band of an exciton couplet associated with the 190-nm EA band observed by Khalil and McGlynn.[7] The sign of this CD band also confirms the z polarization for the 190-nm transition.

The fact that the CD maxima of the 390-nm couplet do not have the same magnitude is due to the additional interaction of the 390-nm transition with the shorter wavelength transitions. These give positive contributions to the rotational strength resulting in slight nonconservative behavior with a larger positive CD maximum at longer wavelength for the CD couplet.

(R)-N-(1-Phenylethyl)- and (R)-N-(1-Phenyl-2,2-dimethylpropyl)-p-nitroaniline [(R)-2 and (R)-3]. For (R)-**2** and (R)-**3** the overall intensity of the CD spectra (Figures 3–5) indicates that the Cotton effects are generated by the electric dipole–dipole coupled oscillator mechanism,[21] the transition of the p-nitroaniline chromophore being coupled to those of the phenyl group. The sign of a particular Cotton effect is determined by the chirality of the coupled oscillators, this chirality depending on the absolute configuration and preferred conformation of the compound and the polarization of the transition moment in the chromophore and in the group to which the latter is coupled. In (R)-**2** and (R)-**3**, the transition moments of the p-nitroaniline chromophore are coupled to the $^1\mathrm{L_a}$ and $^1\mathrm{B_a}$ benzenoid transitions of the phenyl group, the latter moments directed along the phenyl group attachment bond. The $^1\mathrm{L_b}$ and $^1\mathrm{B_b}$ benzenoid transitions, perpendicular to the phenyl group attachment bonds, are deemed ineffective in the generation of Cotton effects due to the relatively unrestricted rotation of the phenyl group about its attachment bond.

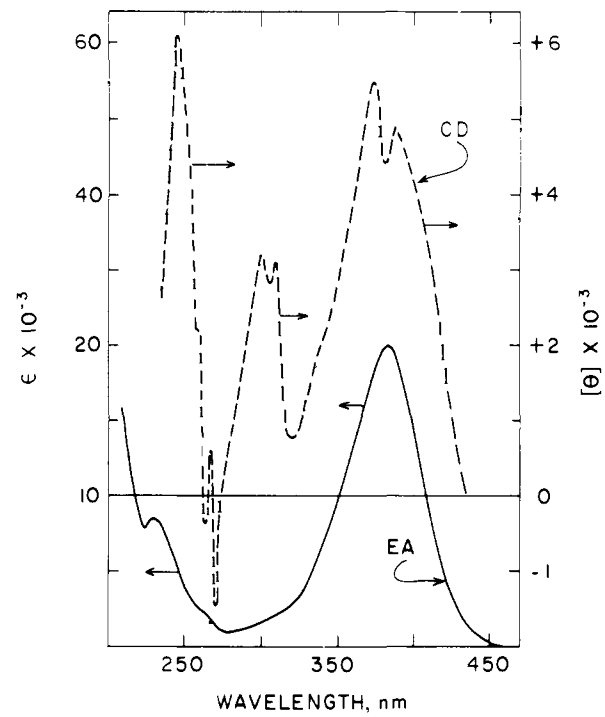


Figure 3. Electronic absorption (EA) and circular dichroism (CD) spectra of (R)-N-(1-phenylethyl)-p-nitroaniline [(R)-**2**] in methanol.

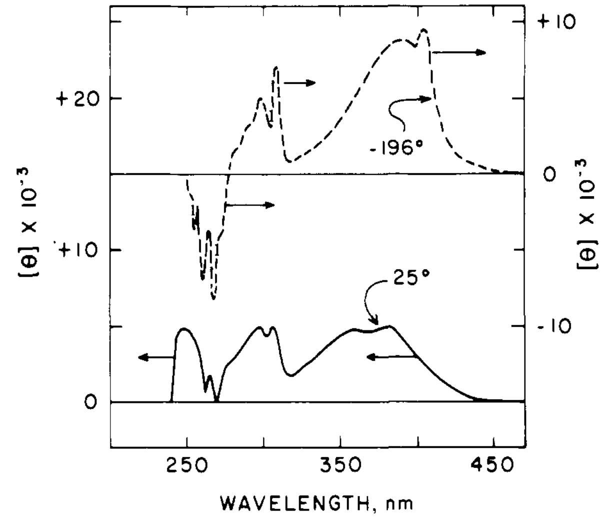


Figure 4. Circular dichroism spectra of (R)-N-(1-phenylethyl)-p-nitroaniline [(R)-**2**] in EPA at 25 and −196 °C.

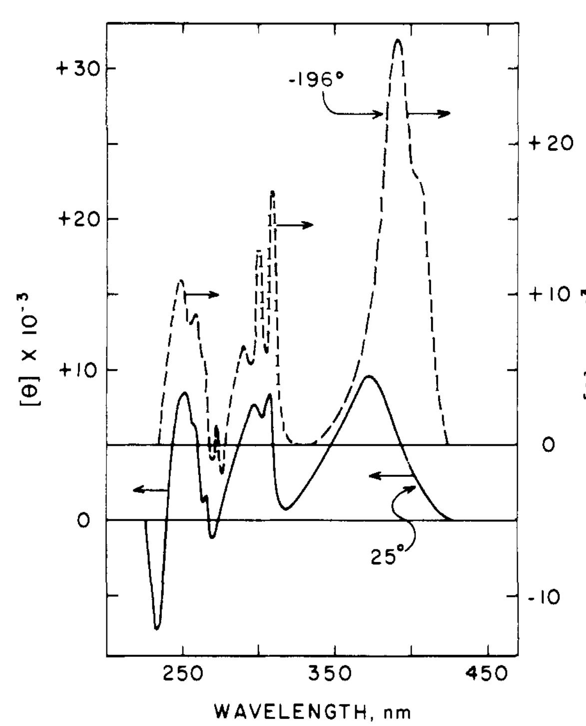
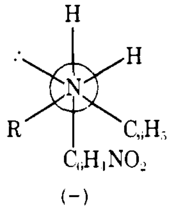
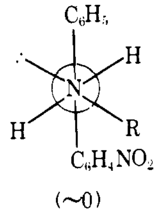


Figure 5. Circular dichroism spectra of (*R*)-*N*-(1-phenyl-2,2-dimethylpropyl)-*p*-nitroaniline [(*R*)-**3**] in EPA at 25 and −196 °C.

Newman projections of the conformers of lowest energy of (*R*)-**2** and (*R*)-**3** may be depicted as **9** and **10, 9a** and **10a, 9b** and **10b,** and **9c** and **10c** being pairs of unresolvable conformational diastereomers of almost equal energy. With each

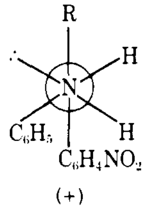


9a



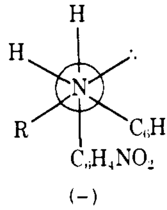
R = CH_3 or $C(CH_3)_3$

9b

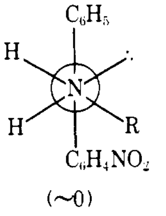


9c

conformer is shown the rotatory contribution associated with a transition of *z* polarization of the *p*-nitroaniline chromophore coupled with the ^1L_a and ^1B_a transitions of the phenyl group.

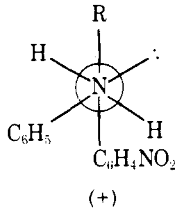


10a



R = CH_3 or $C(CH_3)_3$

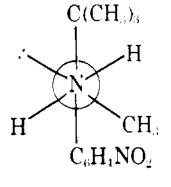
10b



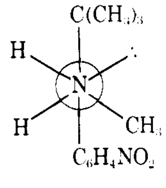
10c

Conformers **9a** and **10a** will be of the highest energy because of steric interaction and will be unimportant compared to the others. Conformers **9b** and **10b** will also contribute negligible rotational strength owing to the near anticolinearity and large separation between the transition moments of the *p*-nitroaniline chromophore and the phenyl group. In **9c** and **10c,** the chirality of the coupled oscillator for *z* polarization of the chromophore is positive, and positive Cotton effects for the 385-nm band are observed. The enhanced CD maxima for (*R*)-**3** as compared to those for (*R*)-**2** are a reflection of the greater steric requirement of a *tert*-butyl group as compared to a methyl group, making **9c** and **10c** more preferred for (*R*)-**3** than (*R*)-**2**.

A similar analysis allows the Cotton effect centered near 385 nm in the spectrum of (*R*)-**1** to be correlated with its absolute configuration. This Cotton effect also arises by the coupled oscillator mechanism,[21] and its sign is determined by the chirality of its transition moment (*z*-polarized) with oscillators in the chiral moiety. Since the polarizability of a carbon-hydrogen bond is negligible compared with that of a carbon-carbon bond,[22,23] only the chirality of the carbon-carbon bond vicinal to the phenyl group-nitrogen bond of the chromophore need be considered when predicting the sign of the Cotton effect. In the rotationally dominant conformers for (*R*)-**1, 11a,** and **11b,** this chirality is negative, and a negative Cotton effect for the 385-nm transition is predicted.



11a



11b

The negative maxima at 263 and 270 nm in the CD spectrum of (*R*)-**2** in methanol may be due to the combined effect of the vibrational modes of the ^1L_b transition of the phenyl group and the 265-nm transition of the *p*-nitroaniline chromophore. Similar negative maxima are not observed in the CD spectrum of (*R*)-**3** in methanol because of the increased intensity of the positive maximum at 246 nm.

In (*R*)-**2** and (*R*)-**3**, the 310- and 260-nm absorption bands give rise to Cotton effects at about 308, 300, and 245 nm, of the same sign as that of the Cotton effect associated with the absorption band near 385 nm, but in (*R*)-**1** the corresponding Cotton effects are opposite in sign to those for the band near 385 nm. This may be due to the circumstance that for (*R*)-**2** and (*R*)-**3**, the nontotally symmetric vibrational progression of the 310- and 265-nm bands of the *p*-nitroaniline chromophore have *z* polarization whose dipolar coupling with the phenyl group transitions becomes more important than the totally symmetric progression whose polarization perpendicular (*x*) to the rotational axis is partially averaged out. This is dramatically demonstrated in the 310-nm band at low temperature where the most intense CD maximum occurs at 308 nm in (*R*)-**2** and (*R*)-**3** (Figures 4 and 5) corresponding to the nontotally symmetric vibronic band origin in (*R*)-**1** at low temperature (Table II). In (*R*)-**2** and (*R*)-**3**, the sign and intensity of the CD maximum at 308 nm follow closely those of the 385-nm band, the former borrowing its intensity from the latter, in agreement with the vibronic theory of circular dichroism.[24] The vibrational fine structure for the 265-nm band can also be seen in the CD spectrum of (*R*)-**1** in EPA at low temperature (Figure 2). Thus, the 250-nm exciton band in (*R*)-**7**, and the 245-nm band in methanol and the 250-nm band in EPA of (*R*)-**2** and (*R*)-**3** may be due to the nontotally symmetric vibronic progression (*z*-polarized) of this band. However, the possibility of an A_1 transition in this region cannot be ruled out.

(*R*)-*N*-[1-(1-Naphthyl)ethyl]-*p*-nitroaniline [(*R*)-4]. In the EA spectrum of (*R*)-**4**, the vibrational progression from 263 to 290 nm and the intense absorption maximum at 223 nm are, respectively, the ^1L_a and ^1B_b transitions of the naphthalene group, parallel and perpendicular, respectively, to its attachment bond.[25] Since the conformers of (*R*)-**4** making the most significant rotatory contributions can be taken as similar to **9c** and **10c,** the close energetic proximity of the 310-nm transition of the *p*-nitroaniline chromophore to the ^1L_a transition

Table III. Eleven Lowest Energy Transitions of *p*-Nitroaniline

	CNDO/S-CI calculation[a]			
symmetry of excited state (transition)	wavelength, nm	oscillator strength	polarization[b]	obsd absorption band, wavelength, nm
$1A_2$ (n → π^*)	456.9			465[c,d]
$1B_2$ (n → π^*)	398.6	4.3×10^{-5}	*y*	429[c] and 391[c,d]
$1B_1$ ($\pi \rightarrow \pi^*$)	282.7	4.1×10^{-3}	*x*	299,[d] ~303-278,[c,e] 308 and 294,[f] 315[c] and 300,[c,g] 289[h]
$2A_1$ ($\pi \rightarrow \pi^*$)	264.1	0.51	*z*	364-370,[d] 323,[e] 385,[f] 392,[g] 337[h]
$2B_1$ ($\pi \rightarrow \pi^*$)	226.8	0.019	*x*	264-273,[d] ~244,[c,e] 250,[c,f] 265[c,g]
$3B_1$ ($\pi \rightarrow \pi^*$)	210.9	0.40	*x*	235,[d] 220-240,[e] 229,[f] 234,[g] 235[h]
$3A_1$ ($\pi \rightarrow \pi^*$)	210.2	3.1×10^{-3}	*z*	227,[g] 219[h]
$4A_1$ ($\pi \rightarrow \pi^*$)	201.6	0.018	*z*	
$2A_2$ ($\sigma \rightarrow \pi^*$)	193.5			
$4B_1$ ($\pi \rightarrow \pi^*$)	189.1	0.31	*x*	200[c,e]
$5A_1$ ($\pi \rightarrow \pi^*$)	188.2	0.86	*z*	190[e]

[a] Thirty configuration interaction states were used. [b] The *z* and *x* axes are the long and short axes, respectively, while the *y* axis is perpendicular to the molecular plane. [c] Shoulder. [d] Single crystal in ref 9. [e] In methylcyclohexane in ref 7. [f] In EPA glass at 77 K in ref 7. [g] Electronic absorption or circular dichroism measurements with (*R*)-**1** in methanol (Table I). [h] Magnetic circular dichroism measurements in heptane-dioxane in ref. 8.

of the naphthyl group suggests that the rotational strength of the former should come mainly from dipolar interaction with the latter. Such an interaction should, for *z* polarization of the 310-nm nontotally symmetric vibronic transitions of the *p*-nitroaniline chromophore, result in positive Cotton effects as are observed. The contribution to the naphthyl group ^1L_a Cotton effects by this interaction should be negative as should the contribution from the dipolar interaction with the intense 385-nm transition of the *p*-nitroaniline group. That the naphthyl group ^1L_a Cotton effects (282-293 nm) are negative indicates that the interaction of this transition with the long-wavelength *z*-polarized (A_1) components near 310 and 385 nm of the *p*-nitroaniline chromophore overshadows that with the more intense but energetically more remote A_1 transition at about 190 nm. This interaction should make a positive contribution to the naphthalene ^1L_a Cotton effects.

The negative sign for the CD maximum at 375 nm, the same sign as that of the ^1L_a naphthalene transition, shows that interaction of the latter with the former cannot be the dominant contribution to its rotational strength. Indeed, the main contribution to the 385-nm rotational strength of (*R*)-**4** comes from dipolar interaction of this A_1 transition of the *p*-nitroaniline chromophore with the intense 223-nm ^1B_b transition of the naphthalene group. This latter transition gives rise to a very strong negative Cotton effect due to dipolar interaction with the strong 190-nm A_1 transition of the *p*-nitroaniline chromophore. The extremely intense Cotton effect of the ^1B_b transition of the naphthyl group implies a preferred conformation of the group about its attachment bond in contrast to the nearly free rotation of the phenyl group in (*R*)-**2** and (*R*)-**3**.

(*R*)-*N*-[1-(2-Furanyl)ethyl]- and (*R*)-*N*-[1-(2-Thienyl)-ethyl]-*p*-nitroaniline [(*R*)-5 and (*R*)-6]. The absorption bands of (*R*)-**5** and (*R*)-**6** at about 225 nm are due to transitions of the furan and thiophene groups, respectively, and the CD spectra can be interpreted in much the same way as those of the (*R*)-*N*-(1-phenylethyl) analog. The positive Cotton effects associated with the 385-, 310-, 255-, and 235-nm *p*-nitroaniline transitions arise by coupling of the A_1 components with the strong $\pi \rightarrow \pi^*$ transitions of the furan and thiophene groups at about 225 nm.[26] Again the transition moment component along the attachment bond of the heterocyclic group is the most effective in inducing dichroic absorption in the *p*-nitroaniline chromophore. On the basis of the conformers similar to **9c** and **10c** being more important than those similar to **9a** and **10a**, positive Cotton effects near 385 and 310 nm are predicted and are observed. This interpretation is complicated by the lack of C_{2v} symmetry for the heterocyclic groups, their near degenerate transitions,[26] and possible exciton splitting with the *p*-nitroaniline transitions in this region.

CNDO/S–CI Calculations. During the course of this research a CNDO/S-CI calculation[27] for *p*-nitroaniline was carried out in order to augment the interpretation of our CD results. It was later learned that Khalil, Seliskar, and McGlynn[7,10] had also carried out exactly the same calculation. The results of the two calculations are essentially identical except the oscillator strengths obtained by Khalil, Seliskar, and McGlynn[10] may be too low by a factor of 2 (cf. ref 28). The present results for the 11 lowest energy transitions for *p*-nitroaniline by the CNDO/S-CI method are given in Table III. Also shown in Table III are the assignments of the symmetry of the various excited states, their polarization, and the experimentally observed absorption maxima. The orderings of the seven lowest energy transitions obtained by the ab initio CI method[9] are somewhat different from those of the present CNDO/S calculation, but the transition energies of the latter are much superior.

A single-crystal experiment[9] revealed an absorption shoulder of very low intensity at 465 nm and two weak ones at 429 and 391 nm. The latter were assigned as two separate B_1 transitions, and the former was assigned to a B_2 transition.[9] Based on the CNDO/S transition energies we prefer to assign the 465-nm absorption to the $1A_2$ transition and the two others to vibronic structure of the $1B_2$ transition, both the $1A_2$ and $1B_2$ excited states arising by n → π^* transitions. It should be noted, however, the Khalil, Seliskar, and McGlynn[10] have argued that these n → π^* transitions should be at higher energies than the lowest energy $\pi \rightarrow \pi^*$ transition.

The present assignment of the n → π^* transition to the lowest energy singlet-singlet transitions is not inconsistent with the luminescence characteristics of *p*-nitroaniline observed by Khalil and McGlynn[7] that the lowest energy transition of *p*-nitroaniline does not fluoresce in nonpolar media and its intensity increases on N-methylation and on increasing solvent polarity. It is well known that a blue shift occurs for an n → π^* transition in polar solvents owing to stabilization of nonbonding orbitals. Since the $2A_1$ transition is one of strong charge transfer with the excited state more polar than the ground state, hydrogen bonding stabilizes the excited state more than the ground state resulting in a red shift of this transition in polar solvents. In fact, this absorption band is shifted more than 5000 cm^{-1} to the red by changing the solvent from methylcyclohexane to EPA.[7] The combined result of these two effects is the possible inversion of states with the $2A_1$

Table IV. N-Substituted *p*-Nitroanilines

				combustion analysis							
				calcd, %				found, %			
compd[a]	mp, °C	$[\alpha]^{25}{}_D$, deg[b]	molecular formula	C	H	N	S	C	H	N	S
(*R*)-**1**[c]	78-80	−84	$C_{12}H_{18}N_2O_2$	64.84	8.16	12.60		65.03	8.40	12.60	
(*S*)-**2**[d]	68-70[e]	−169	$C_{14}H_{14}N_2O_2$	69.40	5.83	11.56		69.59	5.91	11.47	
(*R*)-**3**[f]	171-172	+183	$C_{17}H_{20}N_2O_2$	71.80	7.09	9.85		71.95	7.18	9.90	
(*S*)-**4**[f,g]	131-132[h]	+381	$C_{18}H_{16}N_2O_2$	73.95	5.52	9.58		73.85	5.61	9.65	
(*S*)-**5**[i]	61-62	−319	$C_{12}H_{12}N_2O_3$	62.06	5.21	12.06		62.17	5.32	12.01	
(±)-**6**	132-133[j]	+3	$C_{12}H_{12}N_2O_2S$	58.04	4.87	11.28	12.91	57.91	4.74	11.26	13.01
(*R*)-**6**[k]	85-86	+152									

[a] The characterization of the corresponding amine is given as a footnote. [b] *c* 1.01-1.23 g/100 mL in methanol. [c] Reference 16. [d] Reference 14 for the *R* amine. [e] After molecular distillation at 160 °C (3 mm) over 24 h. [f] Reference 15. [g] The configurational assignment for the corresponding amine has been verified by R. Menicagli, L. Lardicci, and C. Botteghi, *Chem. Ind.* (*London*), 920 (1974). [h] After molecular distillation at 180 °C (0.5 mm) over 8 h. [i] This work. [j] After molecular distillation of (*R*)-**6** at 136 °C over 16 h. A sample prepared from the racemic amine had mp 131-132 °C. [k] Reference 17 for the *S* amine.

$\pi \rightarrow \pi^*$ transition at a lower energy than the $1A_2$ and $1B_2$ $n \rightarrow \pi^*$ transitions with the consequence of fluorescence only in polar solvents.

An alternate assignment is to regard the extremely weak 465-nm absorption band observed by Bertinelli, Palmieri, Brillante, and Taliani[9] as either a singlet-triplet transition or as an artifact[29] and assign the 429- and 391-nm bands as the $1A_2$ and $1B_2$ transitions, respectively. This will make the inversion of states argument above even more persuasive since only small blue shifts are needed to make the $1A_2$ and $1B_2$ transitions higher in energy than the red-shifted $2A_1$ transition in a polar solvent.

It should be noted that molecular orbital calculations by Plotnikov and Komarov[30] also place the singlet $n \rightarrow \pi^*$ transition of *p*-nitroaniline lower in energy than the lowest energy $\pi \rightarrow \pi^*$ transition, albeit the $n \rightarrow \pi^*$ transition at a higher energy than that given by the CNDO/S calculations. Somewhat more quantitative arguments than that presented above in connection with the inversion of states concept are also presented by Plotnikov and Komarov[30] to interpret the luminescence properties of *p*-nitroaniline.

The intense absorption maximum observed at 364-370 nm in the single crystal,[9] 385 nm in polar solvents,[7] and 323 nm in nonpolar solvents[7] is assigned to the $2A_1$ transition and the strong absorption band at about 235 nm[7,9] to the $3B_1$ transition in agreement with previous assignments.[4,6-9] Khalil and McGlynn[7] have assigned the intense 190-nm band which they observed to the $5A_1$ transition. Our CD results confirm this assignment, but the shape of the absorption band reported by Khalil and McGlynn[7] suggests that it may be a composite of the $4B_1$ and $5A_1$ with the former as its long wavelength wing.

Our EA and CD measurements suggest short (x) axis polarized transitions at about 315, 300, and 265 nm. The low-energy pair is assigned to totally symmetric vibrational modes of the $1B_1$ transition and the other to the $2B_1$ transition. Magnetic circular dichroism (MCD) measurements[8] and the CD results indicate a long (z) axis polarized transition at about 225 nm which is identified as the $3A_1$ and/or the $4A_1$ transition. These assignments, with minor exceptions, are in general agreement with those of Khalil, Seliskar, and McGlynn.[7,10]

Experimental Section

Melting points were taken in open capillary tubes and are corrected. Boiling points are also corrected. Optical rotations at the sodium D line were measured using a visual polarimeter and a 1-dm sample tube except for the derivatives of *trans*-1,2-cyclohexanediamine. The latter were measured using a Rudolph Autopol III polarimeter using a 2-dm sample tube. Isotropic electronic absorption (EA) spectra were obtained with a Cary Model 14 spectrometer with the normal variable slit and matched 1-cm cells. Circular dichroism (CD) spectra with methanol as solvent were measured with a Cary Model 60 spectropolarimeter with a CD Model 6001 accessory. The slit was programmed for a spectral band width of 1.5 nm, and cut-off was indicated when the dynode voltage reached 400 V. With EPA as the solvent, the CD spectra were measured using a JASCO Model J-40A spectropolarimeter by Ruth Records at Stanford University. All of the *N*-*p*-nitroanilines (**1**-**8**) and the *N*-salicylidene derivatives of (*S*)-**7** and (*S*)-α-(1-furanyl)ethylamine had ^1H NMR spectra (JEOL JNM-MH-100 operating at 100 MHz) in deuteriochloroform or acetone-d_6 compatible with their assigned structures. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn.

***N*-*p*-Nitroaniline Derivatives 1-6.** A one-third molar equivalent of *p*-fluoronitrobenzene was added to the amine (1.0 g) in dimethyl sulfoxide (5 mL) and the mixture heated at 50 °C for 24-96 h. The solution was diluted with water (50 mL), and the acidity adjusted to pH 4-6 with glacial acetic acid. Refrigeration was used when needed to promote crystallization of the product. The derivative was collected by filtration and recrystallized from benzene-hexane as yellow solids. Some of the derivatives were subjected to molecular distillation. Details and properties are given in Table IV.

Upon prolonged heating during molecular distillation, (*R*)-**6** was racemized as evidenced by the physical properties of the distillate (Table IV). Racemization did not occur on molecular distillation of (*S*)-**2** and (*S*)-**4** since their melting points were the same before and after molecular distillation and, after molecular distillation, had high rotatory powers at the sodium D line. Also, the sample of (*S*)-**2** prior to molecular distillation had $[\alpha]^{25}{}_D$ −159° (*c* 1.20, CH_3OH), slightly lower than that observed after molecular distillation.

(*R*)-*trans*-*N*,*N*′-Di(*p*-nitrophenyl)-1,2-cyclohexanediamine [(*R*)-7]. *p*-Fluoronitrobenzene (0.20 g, 1.4 mmol) was added to (*R*)-*trans*-1,2-cyclohexanediamine[18] (0.20 g, 1.8 mmol) in dimethyl sulfoxide (7 mL) and the mixture stirred at 50 °C for 4 h. To the cooled mixture were added ethyl ether (10 mL) and 0.2 N hydrochloric acid (15 mL). The aqueous layer was separated and the ethereal layer extracted with 0.2 N hydrochloric acid (10 mL). The combined aqueous layers were made basic with 2 N sodium hydroxide (4 mL) and then extracted with ether (3 × 25 mL). This ethereal solution was dried (Na_2SO_4), and evaporation of the solvent gave crude (*R*)-*N*-(*p*-nitrophenyl)-1,2-cyclohexanediamine [(*R*)-**8**] (0.22 g, 67%). To this sample in dimethyl sulfoxide (6 mL) was added *p*-fluoronitrobenzene (0.22 g, 0.16 mmol), and the mixture was stirred at 70 °C for 16 h. The yellow semisolid reaction mixture was cooled and diluted with water (40 mL). This mixture was extracted with ether (3 × 20 mL). The ether was extracted with 0.5 N hydrochloric acid (2 × 15 mL). After drying (Na_2SO_4), evaporation of the ether gave an oil as residue. Addition of ethanol (5 mL) and then carbon tetrachloride (10 mL) gave solid (*R*)-**7** (0.13 g, 39%) which was recrystallized from methanol-carbon tetrachloride: mp 204-206 °C; $[\alpha]^{20}{}_D$ +875° ($[\phi]^{20}{}_D$ +4910°) (*c* 0.192, CH_3OH).

Anal. Calcd for $C_{18}H_{20}N_4O_4 \cdot 4/3CCl_4$: C, 41.36; H, 3.59; Cl, 33.67; N, 9.98. Found: C, 41.23; H, 3.69; Cl, 33.26; N, 9.90.

Recrystallization from chloroform gave (*R*)-**7**: mp 118-120 °C with resolidification at 135 °C and remelting at 203-205 °C; $[\alpha]^{20}{}_D$ +1030° ($[\phi]^{20}{}_D$ +4900°) (*c* 0.0625, CH_3OH).

Anal. Calcd for $C_{18}H_{20}N_4O_4 \cdot CHCl_3$: C, 47.97; H, 4.45; Cl, 22.35; N, 11.78. Found: C, 48.19; H, 4.60; Cl, 22.89; N, 11.80.

Racemic **7** was prepared from the racemic diamine in a similar way and was recrystallized from ethanol–chloroform: mp 236–237 °C.

Anal. Calcd for $C_{18}H_{20}N_4O_4$: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.57; H, 5.65; N, 15.58.

(*S*)-*trans*-*N*-(*p*-Nitrophenyl)-1,2-cyclohexanediamine [(*S*)-8]. *p*-Fluoronitrobenzene (0.80 g, 5.7 mmol) was stirred with (*S*)-*trans*-1,2-cyclohexanediamine[18] (0.60 g, 5.2 mmol) in dimethyl sulfoxide (8 mL) at room temperature for 20 h. The reaction mixture was diluted with water (40 mL) to which was added 2 N hydrochloric acid (2 mL) and then extracted with ether (2 × 100 mL). The aqueous layer was made basic by the addition of 2 N sodium hydroxide and then extracted again with ether (2 × 100 mL). Evaporation of the latter ethereal solution gave a crystalline residue (0.60 g) which was dissolved in hot methanol, cooled, and filtered. The filtrate was evaporated, and treatment of the residue with ethyl acetate–ether (1:1, 20 mL) gave (*S*)-**8** (0.120 g, 10%): mp 136–138 °C. Recrystallization from ethyl acetate–ether gave the analytical sample: mp 137–138 °C; $[\alpha]^{25}_{\mathrm{D}}$ +50° (*c* 0.280, CH_3OH).

Anal. Calcd for $C_{12}H_{17}N_3O_2$: C, 61.26; H, 7.28. Found: C, 60.98; H, 7.33.

Salicylaldehyde (0.10 g, 0.82 mmol) was added to (*S*)-**8** (0.20 g, 0.85 mmol) in methanol (5 mL), and the mixture was stirred at 50 °C for 1 h. Evaporation of the solvent followed by the addition of ethyl acetate–cyclohexane (1:1, 4 mL) gave (*S*)-*trans*-*N*-(*p*-nitrophenyl)-*N'*-salicylidene-1,2-cyclohexanediamine (0.21 g, 75%): mp 145–148 °C. Recrystallization from carbon tetrachloride gave the analytical sample: mp 149–150 °C; $[\alpha]^{20}_{\mathrm{D}}$ +87° (*c* 0.396, CH_3OH).

Anal. Calcd for $C_{19}H_{21}N_3O_3$: C, 67.24; H, 6.24; N, 12.38. Found: C, 67.30; H, 6.27; N, 12.18.

(*S*)-α-(2-Furanyl)ethylamine. The racemic amine was prepared by lithium aluminum hydride reduction[31] of 1-acetylfuran oxime[32] and had bp 70–72 °C (42 mm) and n^{28}_{D} 1.4726 [lit.[32] bp 145–147 °C (740 mm) and n^{20}_{D} 1.4758]. Addition of an equal molar amount of (+)-tartaric acid to the racemic amine in methanol and recrystallization from methanol gave a pure acid tartrate salt: $[\alpha]^{25}_{\mathrm{D}}$ +15° (*c* 2.01, H_2O) [lit.[19] $[\alpha]^{20}_{546}$ +15.29° (*c* 2, H_2O)].[33] Decomposition of this salt in the usual way gave the *S* amine: bp 150 °C (746 nm); α^{25}_{D} −21.8° (neat, 1 dm); $[\alpha]^{25}_{\mathrm{D}}$ −22° (*c* 1.06, CH_3OH) [lit.[19] $[\alpha]^{20}_{\mathrm{D}}$ −22.9° (state not specified)]. Addition of the *S* amine (143 mg, 1.29 mmol) to salicylaldehyde (172 mg, 1.41 mmol) in benzene (7 ml) gave the *N*-salicylidene derivative as a yellow oil: UV max (CH_3OH) 314 (ϵ 4100), 256 (13 000), and 216 nm (27 000); (hexane) 320 (ϵ 4700), 260 (13 000) (sh), 256 (14 000), 216 nm (29 000); CD (*c* 0.0137, CH_3OH) $[\theta]_{410}$ ±0, $[\theta]_{400}$ ±0, $[\theta]_{380}$ +350, $[\theta]_{360}$ ±0, $[\theta]_{317}$ +14 000, $[\theta]_{294}$ ±0; (*c* 0.001 37) $[\theta]_{294}$ ±0, $[\theta]_{276}$ −23 000, $[\theta]_{266}$ ±0, $[\theta]_{255}$ +42 000, $[\theta]_{241}$ ±0, $[\theta]_{235}$ −7500 (sh), $[\theta]_{223}$ −49 000, $[\theta]_{220}$ −38 000; (*c* 0.001 30, hexane) $[\theta]_{400}$ ±0, $[\theta]_{360}$ ±0, $[\theta]_{320}$ +17 000, $[\theta]_{293}$ ±0, $[\theta]_{276}$ −22 000, $[\theta]_{262}$ ±0, $[\theta]_{257}$ +30 000, $[\theta]_{242}$ ±0, $[\theta]_{235}$ −7000 (sh), $[\theta]_{224}$ −40 000, $[\theta]_{220}$ −32 000.

Acknowledgments. We thank the National Science Foundation for generous grants (CHE77-04608 and CHE77-24293) supporting this work and Professor Carl Djerassi, Dr. Edward Bunnenberg, and Ruth Records, Stanford University, for the CD measurements in EPA.

References and Notes

(1) Part 27: H. E. Smith and F.-M. Chen, *J. Org. Chem.*, **44**, 2775 (1979).
(2) Taken in part from the M.A. Thesis of W.I.C., Vanderbilt University, December 1977, and supported by National Science Foundation Grant CHE77-24293.
(3) (a) Vanderbilt University; (b) Tennessee State University and supported by National Science Foundation Grant CHE77-04608.
(4) J. Tanka, *Bull. Chem. Soc. Jpn.*, **36**, 833 (1963).
(5) H. Labhart and G. Wagniere, *Helv. Chem. Acta*, **46**, 1314 (1963).
(6) K. R. Popov, *Opt. Spectrosc.*, **25**, 471 (1968).
(7) O. S. Khalil and S. P. McGlynn, *J. Luminescence*, **11**, 185 (1975/76).
(8) A. Kaito, A. Tajiri, and M. Hatano, *Bull. Chem. Soc. Jpn.*, **49**, 2207 (1976).
(9) F. Bertinelli, P. Palmieri, A. Brillante, and C. Taliani, *Chem. Phys.*, **25**, 333 (1977).
(10) O. S. Khalil, C. J. Seliskar, and S. P. McGlynn, *J. Mol. Spectrosc.*, **70**, 74 (1978).
(11) H. E. Smith, L. J. Schaad, R. B. Banks, C. J. Wiant, and C. F. Jordan, *J. Am. Chem. Soc.*, **95**, 811 (1973).
(12) H. E. Smith, R. K. Orr, and F.-M. Chen, *J. Am. Chem. Soc.*, **97**, 3126 (1975).
(13) Th. J. de Boer and I. P. Dirkx in "The Chemistry of the Nitro and Nitroso Groups", Part 1, H. Feuer, Ed., Interscience, New York, 1969, Chapter 8.
(14) H. E. Smith, S. L. Cook, and M. E. Warren, Jr., *J. Org. Chem.*, **29**, 2265 (1964).
(15) M. E. Warren, Jr., and H. E. Smith, *J. Am. Chem. Soc.*, **87**, 1757 (1965).
(16) H. E. Smith and H. E. Ensley, *Can. J. Chem.*, **49**, 2902 (1971).
(17) H. E. Smith, E. P. Burrows, M. J. Marks, R. D. Lynch, and F.-M. Chen, *J. Am. Chem. Soc.*, **99**, 707 (1977).
(18) H. E. Smith, J. R. Neergaard, E. P. Burrows, and F.-M. Chen, *J. Am. Chem. Soc.*, **96**, 2908 (1974).
(19) A. P. Terent'ev, R. A. Gracheva, and L. F. Titova, *Zh. Obshch. Khim.*, **34**, 513 (1964); *J. Gen. Chem. USSR*, **34**, 516 (1964).
(20) M. Szostak and J. W. Rohleder, *Acta Phys. Pol. A*, **37**, 521 (1970).
(21) J. A. Schellman, *Acc. Chem. Res.*, **1**, 144 (1968).
(22) W. H. Inskeep, D. W. Miles, and H. Eyring, *J. Am. Chem. Soc.*, **92**, 3866 (1970).
(23) P. A. Snyder and W. C. Johnson, Jr., *J. Am. Chem. Soc.*, **100**, 2939 (1978).
(24) O. E. Weigang, Jr., *J. Chem. Phys.*, **43**, 3609 (1965).
(25) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy", Wiley, New York, 1962, p 305.
(26) R. Hakansson, B. Norden, and E. W. Thulstrup, *Chem. Phys. Lett.*, **50**, 305 (1977).
(27) J. Del Bene, H. H. Jaffe, R. L. Ellis, and G. Kuehnlenz, "CNDO/S-CI Molecular Orbital Calculations with Complete Neglect of Differential and Configuration Interaction", Program 174, Quantum Chemistry Program Exchange (QCPE), Indiana University, Bloomington, Ind.
(28) R. L. Ellis, R. Kuehnlenz, and H. H. Jaffe, *Theoret. Chim. Acta*, **26**, 131 (1972).
(29) We thank a referee for suggesting this possibility.
(30) V. G. Plotnikov and V. M. Komarov, *Spectrosc. Lett.*, **9**, 265 (1976).
(31) D. R. Smith, M. Maienthal, and J. Tipton, *J. Org. Chem.*, **17**, 294 (1952).
(32) A. P. Terent'ev and R. A. Gracheva, *Zh. Obshch. Khim.*, **28**, 1167 (1958); *J. Gen. Chem. USSR*, **28**, 1225 (1958).
(33) Evidently the configurational designator for the resolving agent reported in ref 19 is incorrect.