

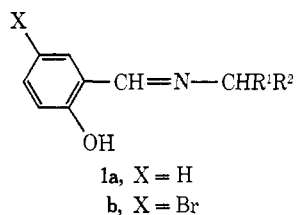
Optically Active Amines. XVI.¹ The Exciton Chirality Method Applied to the Salicylideneimino Chromophore. The Salicylideneimino Chirality Rule

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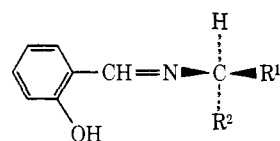
Abstract: The Cotton effects of *N*-salicylidene derivatives of chiral α - and β -arylalkylamines are interpreted in terms of a coupled oscillator mechanism. The exciton splittings in the circular dichroism (CD) spectra of the *N,N'*-di(5-bromosalicylidene) derivative of (*R*)-(-)-*trans*-1,2-cyclohexanediamine and the *N,N'*-di(5-bromosalicylidene) and *N,N'*-disalicylidene derivatives of (*R*)-(-)-1,2-propanediamine are utilized to determine the transition moment directions for the salicylideneimino chromophore. A simple chirality rule is then devised for *N*-salicylidene- β -arylalkylamines, stating that the sign of the Cotton effects near 255 and 315 nm (or the long wavelength band in the case of exciton splitting) is the same as the sign of the chirality (right-handed screw for positive chirality) of the attachment bonds to the aryl and salicylideneimino groups. Agreement is shown with the CD data for β -arylalkylamine derivatives for which the aryl substituent is a phenyl, *p*-nitrophenyl, *p*-hydroxyphenyl, or *p*-chlorophenyl group. For the *N*-salicylidene derivatives of α -arylalkylamines, the sign of chirality is determined by placing the transition moments at the center of the aryl group and of the phenyl ring of the salicylideneimino chromophore. Again positive chirality gives positive Cotton effects near 255 and 315 nm if the interaction energy is positive. Agreement is shown with the CD data for chiral α -arylalkylamine derivatives for which the aryl substituent is a 1-naphthyl, phenyl, 2-pyridyl, or 4-pyridyl group. For the *N*-salicylidene derivatives of chiral alkylamines, the one-electron mechanism accounts for the observed Cotton effects. Consequently, the C_s symmetry of the salicylideneimino chromophore suggests the application of a planar sector rule.

Earlier we proposed a planar sector rule⁴ which correlates the absolute configuration of the *N*-salicylidene derivative (**1a**) of a chiral amine with its



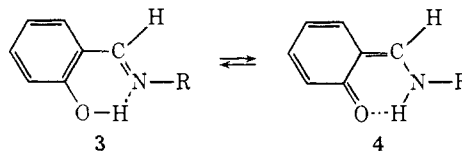
optical rotatory dispersion^{5,6} (ORD) and circular dichroism^{1,4,7-9} (CD) spectra. Initially application of this rule was found for the *N*-salicylidene derivatives of α -(1-naphthyl)ethylamine^{6,7} and a variety of α - and β -phenylalkylamines.⁴⁻⁷ Subsequently, it was shown that the rule also applies to the *N*-salicylidene derivatives of chiral alkylamines,⁸ α -(2- and 4-pyridyl)ethylamine,⁹ norephedrine, and norpseudoephedrine.¹

The electronic (isotropic) absorption (EA) spectra of the *N*-salicylidene derivatives of structure **1a** in methanol or ethanol are typified by that of (*S*)-*N*-salicyli-



(*S*)-**2**, R¹ = CH₃; R² = C₆H₅
 (*S*)-**5**, R¹ = CH₃; R² = CH₂C₆H₅
 (*R*)-**6**, R¹ = C₆H₅; R² = C(CH₃)₃
 (*S*)-**8**, R¹ = CH₃; R² = C₂H₅
 (*R*)-**9**, R¹ = C(CH₃)₃; R² = CH₃

dene- α -phenylethylamine [(*S*)-**2**] (Figure 1 and Table I) which shows maxima in methanol at 215, 255, 283 (shoulder), 315, and 403 nm. The EA spectra of *N*-5-bromosalicylidene derivatives (**1b**) are the same except for positions of the two longest wavelength bands at 328 and 415 nm.⁵ The three bands near 215, 255, and 315 (328) nm are assigned to transitions of the intramolecularly hydrogen-bonded salicylideneimino chromophore (**3**).¹⁰⁻¹³ The band near 400 nm in ethanol or



methanol, which in dioxane is a shoulder with a reduced intensity and in hexane is very weak or absent, and the

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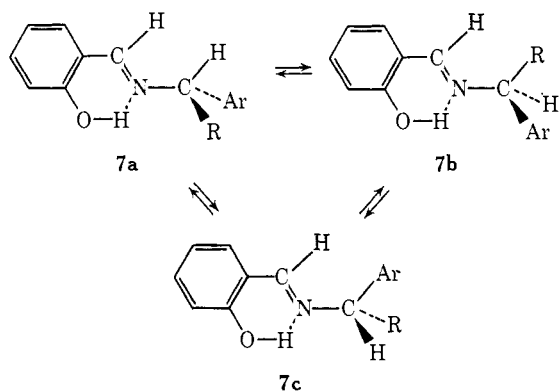
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shoulder near 283 nm, which is not observed in dioxane or hexane,⁵⁻⁸ have been assigned to hydrogen-bonded complexes of the solvent with the derivative¹⁰ or to a tautomeric ketoimine form (4),^{11-13,14} stabilized by and in relatively greater amount in a more polar solvent.

The EA bands near 255, 315 (328), and 400 (415) nm for the derivatives give rise to Cotton effects. That associated with the absorption band near 215 nm is difficult to examine and usually not measured. No Cotton effect was found associated with the shoulder near 283 nm in ethanol or methanol. In some cases, usually with α -arylalkylamine derivatives [see (*S*)-2 in Figure 1 and Table I], a CD maximum near 275 nm is seen even when hexane is the solvent⁷ and is assigned to the $\pi \rightarrow \pi^*$ transition of the aromatic ring of the parent amine. The free bases also show EA in this same spectral region.

The maximum molecular ellipticities ($[\theta]$) of the CD maxima at 254 and 315 (328) nm for α - and β -arylalkylamine derivatives are roughly ten times as great as for chiral alkylamine derivatives. This observation indicates that in the α - and β -arylamine derivatives there is a strong interaction of the π -electron systems of the aryl group and the salicylideneimino chromophore, the chirality of which gives the sign to the observed Cotton effects near 255 and 315 (328) nm. Thus, (*S*)-*N*-salicylidene- α -phenylethylamine [(*S*)-2] (Figure 1 and Table I) and (*S*)-*N*-salicylidene- α -benzylethylamine [(*S*)-5] show strong positive Cotton effects near 255 and 315 nm, while those of (*R*)-*N*-salicylidene- α -phenylneopentylamine [(*R*)-6] are negative.⁷ For each of these compounds, the absolute value of the molecular ellipticity of the CD maximum near 315 nm is increased by about 20% when the temperature is lowered from room temperature to -192° .⁷

These observations are in agreement with a conformational equilibrium for the hydrogen-bonded *N*-salicylidene derivatives represented by 7a-c. Conformer 7a is



that of lowest energy¹⁵ whether the R group is larger or smaller in effective bulk than the Ar group. For an *N*-salicylidene derivative of structure and configuration 7 (Ar is a 1-naphthyl,^{6,7} phenyl,⁵⁻⁷ benzyl,⁵⁻⁷ *p*-hydroxybenzyl,⁶ *p*-chlorobenzyl,¹ 2-pyridyl,⁹ or 4-pyridyl group;⁹ R is an alkyl,^{5-7,9} alkoxy-carbonyl,⁶ or alkoxy-carbonylmethylene group⁶), the Cotton effects near 255 and 315 are positive, for the enantiomer, negative.

For (*S*)-*N*-salicylidene-*sec*-butylamine [(*S*)-8] and (*R*)-*N*-salicylidene-2,2-dimethyl-3-aminobutane [(*R*)-9],

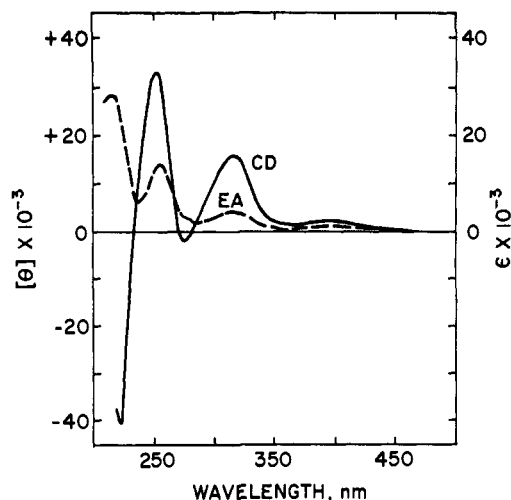


Figure 1. Electronic (isotropic) absorption (EA) and circular dichroism (CD) spectra of (*S*)-*N*-salicylidene- α -phenylethylamine [(*S*)-2] in methanol.

corresponding but less intense CD maxima are observed, positive for (*S*)-8 and negative for (*R*)-9.⁸ Since both (*S*)-8 and (*R*)-9 have preferred conformations similar to 7, and the rotatory perturbation by an ethyl group and by a *tert*-butyl group may be taken to be larger than that of a methyl group,¹⁶ the same planar sector rule for the salicylideneimino chromophore also predicts the sign of the observed Cotton effects. Assuming a similar preferred conformation of the salicylideneimino group about its attachment bond and the same planar sector rule, the sign of the Cotton effect near 315 nm shown by a number of 20-aminopregnanes^{17,18} can be predicted. For cycloalkylamines,¹⁹ contributions from several conformations may be important and perturbations by remote groups may be difficult to assess.¹⁹ In some of these cases, predictions based on the planar sector rule are unreliable.

The planar sector rule was based on empirical observations, and the wide range of its applicability is due to the availability of sufficient model compounds of known configuration. We now wish to account for the sign of the Cotton effects shown by *N*-salicylidene derivatives of chiral aryl-substituted alkylamines and alkylamines using the mechanisms by which Cotton effects are generated.

Three important mechanisms which account for the generation of Cotton effects are well known:²⁰ (1) the one-electron mechanism of Condon, Altar, and Eyring, (2) the coupled oscillator model due to Kuhn and Kirkwood, and (3) the coupling of a magnetic moment of one group with the electric moment of another. The magnitude of the Cotton effects and the general features of the CD spectra of aryl-substituted *N*-salicylidene derivatives indicate that the dominant mechanism operative in these compounds is electric dipole-dipole coupling (mechanism 2). To summarize the relevant expressions for the rotational strength due to this mechanism, consider a molecule consisting of two groups, one having an

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Table I. Spectral Data for *N*-Salicylidene Derivatives

| Compd (solvent) | EA max, λ , nm (ϵ^e) | CD ^a | | | $[\theta]^b = \pm 0$ λ , nm ^d |
|---------------------------|---|---|-------------------------------------|-------------------------------------|---|
| | | Longest and shortest λ , nm ($[\theta]^b$) | Max λ , nm ($[\theta]^b$) | Min λ , nm ($[\theta]^b$) | |
| <i>(S)</i> -2 (MeOH) | | 500 (± 0) | | | 455 |
| | 403 (730) | | 397 (+1,700) | 362 (+1,000) | |
| | 315 (4,000) | | 316 (+16,000) | | |
| | 283 (2,400) ^e | | 275 (-2,300) | | 282 |
| | 255 (14,000) | | 252 (+33,000) | | 270 |
| 215 (28,000) | | 222 (-41,000) | | 234 | |
| <i>(R)</i> -10b (MeOH) | | 215 (-5,000) | | | 470 |
| | | 500 (± 0) | | | |
| | 415 (1,300) | | 415 (-7,600) | 380 (-4,400) | |
| | 328 (6,900) | | 337 (-56,000) | 283 (-2,000) | |
| | 280 (3,100) ^e | | 264 (-99,000) | | 255 |
| 247 (18,000) | | 247 (+110,000) ^e | | | |
| 222 (62,000) | | 233 (+430,000) | | 224 | |
| | | 217 (-220,000) | | | |
| <i>(R)</i> -10b (hexane) | | 208 (-71,000) | | | 375 |
| | | 500 (± 0) | | | |
| | 334 (7,900) | | 342 (-74,000) | 280 (-4,300) | |
| | 263 (13,000) | | 265 (-120,000) | | |
| | 256 (16,000) | | 249 (+120,000) ^e | | 257 |
| 250 (16,000) | | 235 (+550,000) | | | |
| 232 (47,000) ^e | | 226 (+120,000) | | | |
| 225 (58,000) | | 500 (± 0) | | | |
| <i>(R)</i> -11b (MeOH) | | 500 (± 0) | | | 470 |
| | 414 (1,400) | | 415 (-2,700) | 375 (-1,900) | |
| | 328 (6,800) | | 336 (-24,000) | | |
| | 280 (3,100) ^e | | 263 (-51,000) | 282 (± 0) | |
| | 254 (19,000) | | 247 (+37,000) ^e | | 254 |
| 247 (19,000) | | 232 (+190,000) | | | |
| 222 (59,000) | | 216 (-170,000) | | 223 | |
| <i>(R)</i> -11b (hexane) | | 211 (-110,000) | | | 370 |
| | | 500 (± 0) | | | |
| | 334 (8,300) | | 343 (-41,000) | 279 (± 0) | |
| | 263 (16,000) | | 265 (-81,000) | | |
| | 256 (17,000) | | 247 (+65,000) ^e | | 256 |
| 249 (16,000) ^e | | 235 (+320,000) | | | |
| 232 (53,000) ^e | | 224 (± 0) | | | |
| <i>(R)</i> -11c (MeOH) | | 500 (± 0) | | | 460 |
| | 405 (1,300) | | 402 (-3,200) | 366 (-2,200) | |
| | 316 (7,700) | | 322 (-34,000) | 280 (-1,400) | |
| | 282 (4,600) ^e | | 263 (-41,000) | | 254 |
| | 256 (22,000) | | 246 (+55,000) | 236 (+34,000) | |
| | | 226 (+110,000) | | 217 | |
| | | 216 (-23,000) | | | |
| <i>(R)</i> -11c (hexane) | | 500 (± 0) | | | 370 |
| | 214 (44,000) | | 328 (-84,000) | 276 (-5,400) | |
| | 321 (9,300) | | 265 (-100,000) | | |
| | 262 (23,000) | | 248 (+82,000) | 237 (+38,000) | 254 |
| | 256 (25,000) | | 229 (+200,000) | | |
| 250 (21,000) ^e | | 225 (+130,000) | | | |
| 221 (43,000) | | | | | |

Table I (Continued)

| Compd (solvent) | EA max, λ , nm (ϵ^e) | CD ^a | | | $[\theta]^b = \pm 0$ λ , nm ^d |
|---------------------------|---|---|-------------------------------------|-------------------------------------|---|
| | | Longest and shortest λ , nm ($[\theta]^b$) | Max λ , nm ($[\theta]^b$) | Min λ , nm ($[\theta]^b$) | |
| (S)-21 (abs EtOH) | | 500 (± 0) | | | 460 |
| | 418 (420) | | 415 (+1,200) | 385 (+810) | |
| | 326 (4,500) | | 327 (+23,000) | | 296 |
| | | | 291 (-3000) | | |
| | 277 (12,000) ^e | | 266 (+25,000) | | 285 |
| | 258 (16,000) | | 252 (-21,000) | | 260 |
| (S)-22 (abs EtOH) | 220 (39,000) | | | | 224 |
| | | 217 (+9,400) | | | |
| | | 500 (± 0) | | | 465 |
| | 423 (950) ^e | | 408 (+3,400) | 398 (+3,300) | |
| | 344 (13,000) | | 335 (+22,000) | | |
| | 324 (13,000) | | | | |
| | 310 (12,000) | | 296 (-6,300) | | 311 |
| | | | | | 278 |
| L-23 (MeOH) | 271 (12,000) ^e | | 262 (+29,000) | | 249 |
| | 260 (16,000) ^e | | 235 (-40,000) | | |
| | 225 (56,000) | | | | |
| | | 210 (± 0) | | | 450 |
| | | 500 (± 0) | | | |
| | 406 (260) | | 406 (-870) | 370 (-650) | |
| | 319 (3,800) | | 317 (-17,000) | | |
| | 286 (2,900) ^e | | | 286 (-3,900) | |
| 256 (12,000) | | 261 (-48,000) | | 240 | |
| 220 (34,000) ^e | | 228 (+18,000) | | | |
| | | 215 (-7,600) | | | |

^a c 1.07×10^{-4} to 2.76×10^{-2} g/100 ml; length 1 cm; temperature 25–28°. ^b Molecular ellipticity. ^c Molar absorptivity. ^d Each first entry at a longer wavelength than a maximum indicates the interval from the longest wavelength examined for which $[\theta] = \pm 0$. ^e Shoulder.

electronic transition to state a at λ_{1a} and the other having the transition to state b at λ_{2b} . The corresponding transition moments μ_{1a} and μ_{2b} are separated by a distance R_{12} as depicted in Figure 2. The rotational strength R_{1a} of the transition centered at wavelength λ_{1a} as a result of coupling with μ_{2b} can be shown²¹ to be

$$R_{1a} = \frac{2\pi}{c} \frac{V_{12}^{ab}}{h} \frac{\lambda_{1a}\lambda_{2b}}{(\lambda_{1a}^2 - \lambda_{2b}^2)} [\mathbf{R}_{12} \cdot \boldsymbol{\mu}_{1a} \times \boldsymbol{\mu}_{2b}]$$

where $\mathbf{R}_{12} = \mathbf{R}_2 - \mathbf{R}_1$ and

$$V_{12}^{ab} = \frac{\boldsymbol{\mu}_{1a} \cdot \boldsymbol{\mu}_{2b}}{R_{12}^3} - \frac{3(\boldsymbol{\mu}_{1a} \cdot \mathbf{R}_{12})(\boldsymbol{\mu}_{2b} \cdot \mathbf{R}_{12})}{R_{12}^5}$$

The analogous expression for R_{2b} is obtained by interchanging the notations 1 with 2 and a with b. If $\mathbf{R}_{12} \cdot \boldsymbol{\mu}_{1a} \times \boldsymbol{\mu}_{2b}$ is positive (right-handed screw) and the dipolar interaction energy V_{12}^{ab} also positive, the Cotton effect for the longer wavelength band will be positive; for the shorter wavelength band the Cotton effect will be negative and of equal intensity. This type of S-shaped CD spectrum, sometimes referred to as a couplet, is characteristic of a dipolar coupling mechanism. This mechanism will be important when the two bands are close and each has a sizable transition moment.

If the two groups are identical, the excited states are degenerate and the two chromophores participate equally in the transitions. According to exciton theory,^{22,23} the dipolar interaction will split the molecular excited states into two, A and B, with energies

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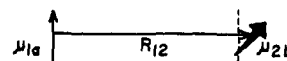


Figure 2. Sense of a right-handed screw is shown for the transition moments separated by a distance R_{12} . $\mathbf{R}_{12} = \mathbf{R}_2 - \mathbf{R}_1$ is a vector directing from 1 to 2. $\mathbf{R}_{12} \cdot \boldsymbol{\mu}_{1a} \times \boldsymbol{\mu}_{2b} = +$ for positive chirality as shown.

$E(A) = E_0^a + V_{12}^{aa}$ and $E(B) = E_0^a - V_{12}^{aa}$ where E_0^a is the energy of state a of a single group. The corresponding expressions for the rotational strength are given by

$$R \begin{pmatrix} A \\ B \end{pmatrix} = \mp \left(\frac{\pi}{2\lambda_{1a}} \right) \mathbf{R}_{12} \cdot \boldsymbol{\mu}_{1a} \times \boldsymbol{\mu}_{2a}$$

The minus sign corresponds to the A coupling mode and the positive sign to the B coupling mode. When a molecule has a C_2 symmetry, A and B represent the in-phase and out-of-phase coupling modes, respectively. Again if $\mathbf{R}_{12} \cdot \boldsymbol{\mu}_{1a} \times \boldsymbol{\mu}_{2a}$ and V_{12}^{aa} are positive, the B coupling mode will occur at longer wavelength with a positive Cotton effect, and a negative band of equal intensity at shorter wavelength will correspond to the A mode.

It is thus clear that a knowledge of the transition moment vectors will enable one to devise a simple chirality rule for unambiguous determination of absolute configuration provided that the dominant mechanism is dipolar coupling. Successful application of the benzoate chirality rule²⁴ is a notable example. For the *N*-salicylidene chromophore, however, the transition

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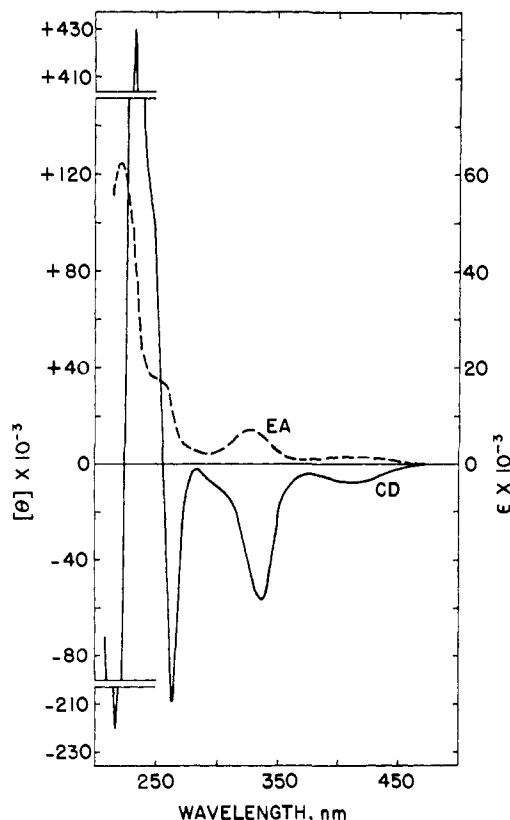


Figure 3. Electronic (isotropic) absorption (EA) and circular dichroism (CD) spectra of (*R*)-*trans*-*N,N'*-di(5-bromosalicylidene)-1,2-cyclohexanediamine [(*R*)-**10b**] in methanol.

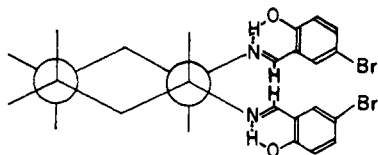
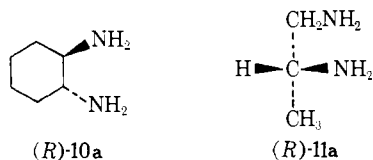


Figure 4. Preferred conformation of *N,N'*-di(5-bromosalicylidene)-1,2-cyclohexanediamine [(*R*)-**10b**].

moment directions are not known. Consequently, we now have utilized the exciton splittings in the CD spectra of the *N,N'*-di(5-bromosalicylidene) derivative²⁵ of (–)-*trans*-1,2-cyclohexanediamine^{26,27} (**10a**) and the



N,N'-di(5-bromosalicylidene) and *N,N'*-disalicylidene derivatives of (–)-1,2-propanediamine²⁸ (**11a**) to assist in determining the transition moment directions for the

(25) The CD spectra of the disalicylidene and di(5-bromosalicylidene) derivatives are essentially the same (Table I). The 5-bromo derivatives, however, have higher melting points⁵ and are in general more readily crystalline.

(26) Signs in parentheses refer to rotatory powers observed with sodium D-light for the amine hydrochlorides in water and for the amines in benzene.

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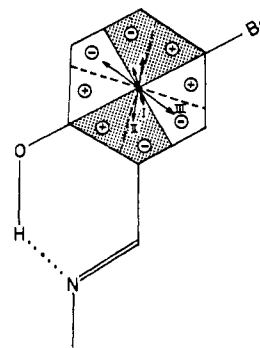


Figure 5. Assigned transition moment directions for bands I, II, and III and the sign of the rotational strength for the B coupling mode. For transition moments in the shaded regions, the B coupling mode is energetically favored over the A coupling mode and thus will occur at longer wavelength.

salicylideneimino chromophore. Both (–)-**10a** and (–)-**11a** have the (*R*) configuration.²⁹

Results and Discussion

(*R*)-*trans*-*N,N'*-Di(5-bromosalicylidene)-1,2-cyclohexanediamine [(*R*)-**10b**]. The EA spectrum for (*R*)-**10b** in methanol (Figure 3 and Table I) displays a weak broad band at 415 nm, a broad and moderately strong band around 328 nm, a shoulder at 280 nm, a broad, strong band at 247 nm, and an intense band at 222 nm. The CD curve (Figure 3 and Table I) consists of two negative Cotton effects at 415 and 337 nm and exciton splittings centered at 255 and 224 nm. The band at 415 nm and the shoulder at 280 nm in the EA spectrum disappear in hexane solution as expected (Table I). On the basis of the similarity of the EA spectrum to that of salicylaldehyde,³⁰ the 328- and 247-nm bands may be attributed to charge-transfer transitions and the 222-nm band to a benzoid transition.³¹ The three bands are hereinafter referred to as bands I, II, and III, respectively. The preferred conformation for (*R*)-**10b** is shown in Figure 4. The energetically favored regions as well as the signs of the rotational strength for the B coupling modes for this conformation are given in Figure 5. For transition moments in the shaded regions of Figure 5, the B coupling mode is energetically favored over the A coupling mode; and thus the B mode will have a lower energy and transitions corresponding to this coupling mode will occur at a longer wavelength than those corresponding to the A mode. The assumed directions of the transition moments for each band are also shown in Figure 5. The signs for the B mode Cotton effects indicated in Figure 5 were obtained by inspection of Dreiding models and the absolute configuration and conformation shown in Figure 4. The rotational strength of the B coupling mode for a transition centered at λ_{1a} is given by

$$R_B = (\pi/2\lambda_{1a})\mathbf{R}_{12} \cdot \mathbf{u}_{1a} \times \mathbf{u}_{2a}$$

Thus the sign of R_B depends on the sign of $\mathbf{R}_{12} \cdot \mathbf{u}_{1a} \times \mathbf{u}_{2a}$ which is positive if the chirality of the two transition moments is positive and negative otherwise. A simple way to obtain the sign is to place the transition moments of assigned direction at the centers of the phenyl rings

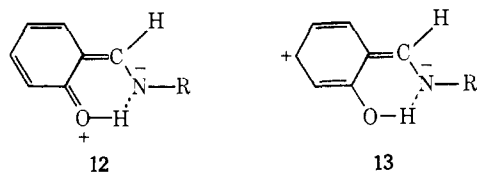
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(31) J. Tanaka and S. Nagakura, *J. Chem. Phys.*, **24**, 1274 (1956).

and then to look through both centers with the arrowhead of the first transition moment (closer to the eye) pointing up. If the arrowhead of the second transition moment lies on the right, the chirality is positive.

The polarization assignments for the 5-bromosalicylideneimine chromophore and also for the salicylideneimine chromophore are based in part on earlier work¹⁰ in which bands I and II for the *N*-salicylideneimine chromophore were assigned to transitions to excited states **12**



and **13**, respectively. In analogy to the charge-transfer band in the benzoate group,³² the transition moment direction for band II has been assigned to be from the center of the benzene ring to the center of the azomethine (C=N) bond.

With the help of Figure 5 one can readily see that the polarization assignments will produce for band II, as is observed, exciton splitting with a negative maximum at the longer wavelength corresponding to the B mode and for band III exciton splitting with a positive maximum at the longer wavelength corresponding to A mode. The assignment for the exciton splitting of band II is in conformity with the generalization of Hug and Wagniere³³ that the longer wavelength portion of the CD spectrum of chromophores of symmetry C_2 will lead to negative Cotton effects for transitions of symmetry B and positive ones for those of symmetry A, if the sense of screw is left handed as in the preferred conformation of (*R*)-**10b** (Figure 4).

The fact that the two exciton bands associated with a given absorption do not have equal areas can be attributed to configuration interaction.²³ Thus, if two bands are close in energy, interaction between them will cause mixing of the molecular excited states. Generally, the symmetric A modes will mix among themselves as will the antisymmetric B modes to produce an increase in magnitude for one mode in one band with a corresponding decrease in magnitude for the same mode in the other band, conversely for the other mode.

The CD band for (*R*)-**10b** around 337 nm is negative with no sign of exciton splitting. This is puzzling in view of the fact that the maximum molar absorptivity is 6900, indicating a $\pi \rightarrow \pi^*$ transition. This may be a consequence of the configuration interaction mentioned above. Assuming that there was an exciton splitting for band I, from the assigned polarization direction in Figure 5, one would predict a negative maximum at longer wavelength corresponding to the B mode. The configuration interactions will mix the B mode of band I with the B mode of bands II and III and the A modes will be similarly mixed among themselves. Thus it is conceivable that both interactions will increase the absolute magnitude of the B mode and decrease the magnitude of the A mode to such an extent that only a single negative Cotton effect is observed for band I.

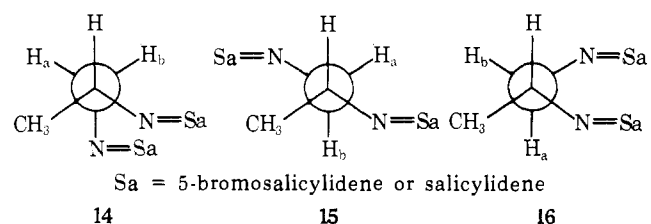
Other possible explanations for the absence of exciton

splitting in band I such as weak exciton coupling as a result of vibrational effect cannot be ruled out. In fact, the weak coupling condition $2V_{12} \ll \Delta$ (Δ is the band width) of Simpson and Peterson³⁴ is satisfied if one estimates $2V_{12}$ from the exciton splitting of band II with proper adjustment. The large Cotton effect associated with this band could then be a result of dipolar as well as magnetic-electric interactions with the other two strong bands.

Dramatic enhancements for the three major CD bands for (*R*)-**10b** are observed in hexane, with accompanying disappearance of the 415-nm band and the 280-nm shoulder in the EA spectrum. This effect may be due to certain conformational changes or more likely the result of tautomerism. The disappearance of both EA bands indicates that the compound exists as pure enolimine (**3**) in hexane solution. The intensity enhancement can be understood if one assumes an equilibrium constant of about one quarter for the tautomerism of **3** to **4** in methanol.

(*R*)-*N,N'*-Di(5-bromosalicylidene)- and (*R*)-*N,N'*-Di-salicylidene-1,2-propanediamine [(*R*)-**11b** and (*R*)-**11c**]. The EA and CD spectra of both (*R*)-**11b** and (*R*)-**11c** in methanol and hexane are very similar in shape to those of (*R*)-**10b** (Table I). However, the open-chain derivatives show maxima of smaller molecular ellipticity which is explained by analysis of their conformational mobility.

Newman projections of the six conformers of lowest energy for (*R*)-**11b** and for (*R*)-**11c** are shown as **14**–**16**. Each projection represents two conformers of about equal energy. For each conformer, the azomethine hydrogen atom of the salicylideneimine moiety at C-2 eclipses the hydrogen atom at C-2 and the other azomethine hydrogen atom eclipses one or the other hydrogen atoms (H_a or H_b) at C-1. The conformers are thus referred to as **14a** and **14b**, **15a** and **15b**, and **16a** and **16b**, respectively.



As suggested by Brewster,³⁵ **14a** and **14b** will be of higher energy due to steric interaction and will be unimportant compared to the other four. Conformers **15a** and **15b** will also contribute negligible rotational strength to the CD spectrum due to the near anti-colinearity and/or large separation between the transition moments of the salicylideneimine groups.

Conformers **16a** and **16b**, the former similar to that shown in Figure 4 for (*R*)-**10b**, are the principal contributors to the CD spectrum. Since the transition moments for band I and II for the chromophores can be regarded as essentially parallel to their attachment bonds, the orientation of the chromophores about their attachment bonds will have little effect on the strength of the CD maxima associated with the transitions near 255 and 315 (328) nm. Conformers **16a** and **16b** should

(32) J. Tanaka, *Bull. Chem. Soc. Jap.*, **36**, 833 (1963).

(33) W. Hug and G. Wagniere, *Tetrahedron*, **28**, 1241 (1972).

(34) W. T. Simpson and D. L. Peterson, *J. Chem. Phys.*, **26**, 588 (1957).

(35) J. H. Brewster, *J. Amer. Chem. Soc.*, **81**, 5475 (1959).

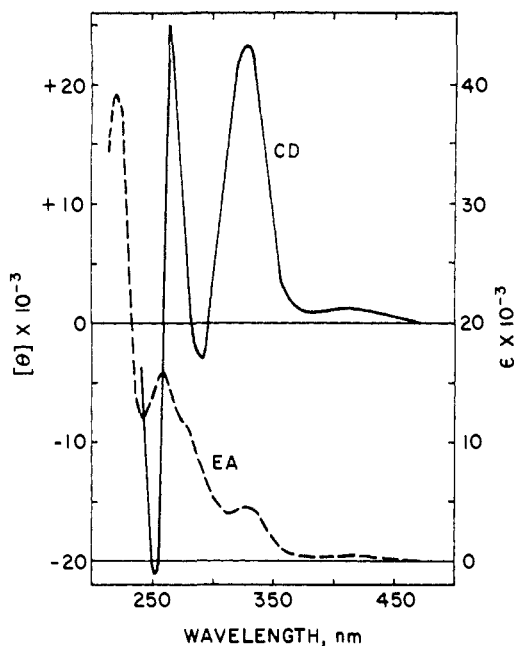
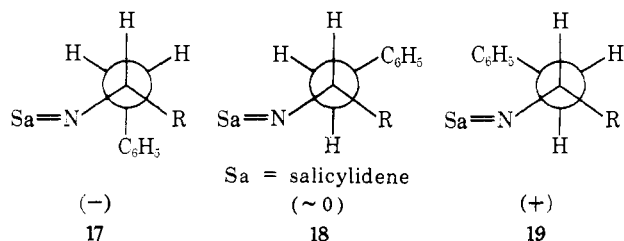


Figure 6. Electronic absorption (EA) and circular dichroism (CD) spectra of *(S)*-*N*-(5-bromosalicylidene)- α -(*p*-nitrobenzyl)ethylamine [(*S*)-21] in absolute ethanol.

both show Cotton effects similar to (*R*)-10b at these wavelengths. In 16a, orientation of the transition moments for band III is the same as that in (*R*)-10b, but in 16b, the orientations will be such that their interaction energy will be nearly zero. Hence 16b will make essentially no contribution to the CD maxima associated with the transition near 215 nm.

***N*-Salicylidene- β -phenylalkylamines.** With the polarization assignments shown in Figure 5 one can now proceed to correlate the absolute configuration of the *N*-salicylidene derivative of a chiral β -phenylalkylamine with the sign of the CD maxima near 255 and 315 nm, assuming a coupled oscillator mechanism. These Cotton effects are the result of interaction with the 1L_a and ${}^1B_{a,b}$ benzenoid transitions of the phenyl chromophore which lie below 255 nm. The effective direction of their respective transition moments is along the phenyl group attachment bond.³⁶

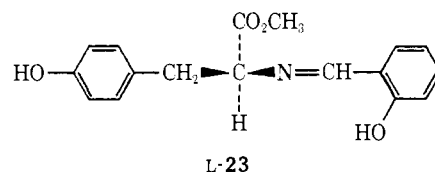
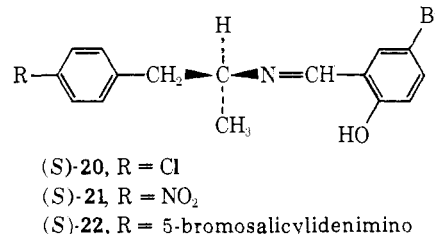
Newman projections of the three conformations of lowest energy for an (*S*)-*N*-salicylidene- β -phenylalkylamine are shown as 17–19. With each is shown the



sign of the corresponding Cotton effect for the bands near 255 and 315 nm. These signs can be easily determined if the transition moment directions for both the salicylidene chromophore and phenyl group

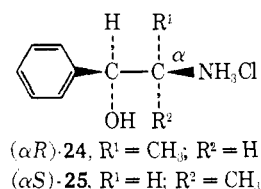
(36) ${}^1B_{a,b}$ has a transition moment with components both along and perpendicular to the phenyl group attachment bond. The interaction due to the perpendicular component will be averaged out due to the phenyl group rotation about its attachment bond and thus will be ineffective.

are away from their respective attachment bonds. The interaction energy will be positive and the sign of the CD maxima will be determined by the chirality of the two attachment bonds, right-handed screw giving positive and left-handed screw giving negative. Again conformer 19 will dominate the CD spectrum, and *N*-salicylidene derivatives of β -phenylalkylamines of the configuration shown as 17–19 will display positive Cotton effects near 255 and 315 nm. This prediction is borne out by all open-chain β -phenyl substituted compounds studied so far,^{5–7} including (*S*)-*N*-(5-bromosalicylidene)- α -(*p*-chlorobenzyl)ethylamine¹ [(*S*)-20], the



previously unreported (*S*)-*N*-(5-bromosalicylidene)- α -(*p*-nitrobenzyl)ethylamine [(*S*)-21] and (*S*)-*N,N'*-di(5-bromosalicylidene)- α -(*p*-aminobenzyl)ethylamine [(*S*)-22], and methyl *N*-salicylidene-*L*-tyrosinate [L-23] whose ORD spectrum was recorded earlier⁶ and whose CD spectrum is recorded now (Table I). (*S*)-21 exhibits exciton splitting for the 255-nm band (Figure 6) since the *p*-nitrobenzyl chromophore in ethanol has a charge-transfer band (1L_a transition) very close to 260 nm.³⁷ The small negative CD band at 291 nm in the CD spectrum of (*S*)-21 and at 296 nm in that of (*S*)-22 (Table I) is attributed to 1L_b transition of the phenyl chromophore of the amine moiety.

The chirality rule also explains the observation that the *N*-(5-bromosalicylidene) derivatives of (αR)-(+)-norephedrine hydrochloride [(αR)-24] and (αS)-(+)-

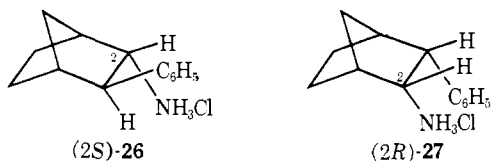


norpseudoephedrine hydrochloride [(αS)-25] display nearly enantiomorphic CD curves at wavelengths longer than 240 nm.¹ The contiguous asymmetric center at the β -carbon atom has only a minor effect on the observed CD maxima near 255 and 328 nm, since the chirality of the *N*-salicylideneimino and phenyl chromophore attachment bonds is the decisive factor.

***N*-Salicylidene Derivatives of *exo*- and *endo*-3-Phenyl-*endo*-2-norbornanamines.** The earlier assignment of the (2*S*) configuration to (+)-*exo*-3-phenyl-*endo*-2-norbornanamine hydrochloride³⁸ [(+)-26], made on the

(37) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, pp 266 and 267.

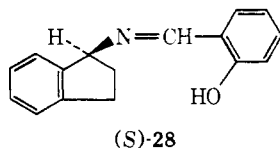
(38) H. E. Smith and T. C. Willis, *Chem. Commun.*, 873 (1969).



basis of the planar sector rule, while not unambiguous, was later confirmed by chemical work.³⁹ When the present chirality rule is applied to the *N*-salicylidene derivative of (+)-26, it is easily seen with a Dreiding model that the chirality is positive for the (2*S*) configuration.

Application to the case of the *N*-salicylidene derivative of (–)-endo-3-phenyl-endo-2-norbornanamine hydrochloride [(–)-27], previously assigned the (2*R*) configuration,³⁸ is complicated by the fact that the attachment bonds to the phenyl and *N*-salicylideneimino groups are almost colinear when the Newman projection is applied along the C(2)–C(3) bond. Using the Dreiding model for (2*R*)-27 and placing the transition moment at the centers of both of the phenyl rings and along the long axes, a negative, albeit small, chirality results. Thus, the observed smaller negative Cotton effects at 255 and 315 nm for the *N*-salicylidene derivative of (–)-27 are accounted for.⁴

***N*-Salicylidene- α -arylalkylamines.** Again the interaction energy and the chirality of the transition moments are the factors determining the signs of Cotton effects. If the transition moments are directed away from the asymmetric carbon atom, the interaction energy will always be positive. However, in determining the chirality, the transition moments should be situated at the centers of the benzene rings since both chromophores are attached to the same carbon atom. The preferred conformation represented by 7a gives positive chirality. Thus positive Cotton effects at 255 and 315 nm are observed for the *N*-salicylidene derivatives of α -arylalkylamines with this absolute configuration. Compounds included are various *N*-salicylidene derivatives of chiral α -phenylalkylamines,^{4–7} α -(1-naphthyl)ethylamine,^{6,7} α -(2- and 4-pyridyl)ethylamine,⁹ as well as (*S*)-*N*-salicylidene-1-indanamine⁴ [(*S*)-28].



The CD spectrum of (*S*)-*N*-salicylidene- α -phenylethylamine [(*S*)-2] is shown in Figure 1. The small negative Cotton effect at 275 nm is attributed to the ¹L_b transition of the phenyl chromophore of the amine moiety. The presence of this CD band indicates that the rotational averaging process for the short axis polarization is not complete. Enhancement of the band in the CD spectrum of (*S*)-28 lends some support to this contention.

Conclusions

The observed Cotton effects in the CD spectra of the *N*-salicylidene derivatives of α - and β -arylalkylamines can be accounted for by the coupled oscillator model.

(39) H. T. Thomas and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 6292 (1970).

A knowledge of relative orientations of transition moments thus enables one to correlate the CD spectrum with the absolute configuration of a derivative unambiguously. The salicylideneimino chirality rule can be stated as follows: for the *N*-salicylidene derivatives of a β -arylalkylamine the sign of the Cotton effect near 255 and 315 nm (or the long wavelength band in the case of exciton splitting) is the same as the sign of the chirality (right-handed screw for positive chirality) of the attachment bonds to the aryl and salicylideneimino groups. For the *N*-salicylidene derivatives of α -arylalkylamines, however, the attachment bonds of both the aryl group and the salicylideneimino group originate from the same carbon atom. Thus the sign of chirality is determined by placing the transition moments at the center of the aryl group and of the phenyl ring of the salicylideneimino chromophore. Again positive chirality gives positive Cotton effects near 255 and 315 nm if the interaction energy is positive. The determination of absolute configuration by the chirality of transition moments has an advantage over the previously proposed sector rule in that no model compounds are needed. For the *N*-salicylidene derivatives of chiral alkylamines, the one-electron mechanism accounts for the observed Cotton effects.⁸ Consequently, the C_s symmetry of the salicylideneimino chromophore suggests the application of the planar sector rule⁴⁰ as outlined earlier.⁸

Experimental Section

The *N*-salicylidene and *N*-(5-bromosalicylidene) derivatives were prepared as previously reported.⁵ Melting points were taken in open capillary tubes and are corrected. Optical rotatory power measurements at the sodium D line were obtained using a visual polarimeter and a 1-dm sample tube or, as noted, a 2-dm tube. Electronic absorption (EA) spectra were measured with a Cary Model 14 spectrophotometer using matched 1-cm cells and the normal variable slit. Circular dichroism (CD) spectra were observed with a Cary Model 60 spectropolarimeter equipped with a CD Model 6001 accessory. The slit was programmed for a spectral bandwidth of 1.5 nm and a 1-cm cell was used. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn.

(*S*)-*N*-Salicylidene- α -phenylethylamine [(*S*)-2] was recrystallized from methanol: mp 74–75°, [α]_D²⁵ +185° (c 1.17, CH₃OH) [lit.⁵ mp 75–76°, [α]_D²⁵ +188° (c 1.2, CH₃OH)].

(*R*)-(–)-*trans*-1,2-Cyclohexanediamine [(*R*)-10a]. Predominantly (±)-*trans*-1,2-cyclohexanediamine sulfate⁴¹ was prepared from the commercially available mixture of *cis* and *trans* diamines and was resolved using a modification of a previously reported procedure.⁴² Barium hydroxide octahydrate (74.3 g, 0.235 mol) was added to a slurry of (±)-*trans*-1,2-cyclohexanediamine sulfate (50.0 g, 0.236 mol) in water (250 ml). The mixture was heated on a steam bath with stirring for 1 hr, cooled, and filtered through Celite. (+)-Tartaric acid (35.4 g, 0.236 mol) was added to the filtrate, and this solution was heated on a steam bath for 0.5 hr, then cooled in an ice-salt mixture. The (+)-tartaric acid salt of (–)-10a (10.4 g) precipitated as fine, white granules, [α]_D²⁵ +13° (c 0.40, H₂O, 2-dm). After one recrystallization from water the salt had [α]_D²⁵ +12° (c 0.40, H₂O, 2-dm) [lit.⁴³ [α]_D +11.5° (c 1%, H₂O)]. Decomposition of the salt with sodium hydroxide gave (–)-10a which was extracted into benzene, [α]_D²⁵ –41.8° (c 1.4, C₆H₆, 2-dm) [lit.²⁷ [α]_D¹⁵ –42.6° (C₆H₆)]. The concentration of (–)-10a in benzene was determined by titration with 0.101 *N* hydrochloric acid²⁸ using methyl orange as the indicator. Tris(hydroxymethyl)amino-methane⁴⁴ was used as the primary standard for the acid.

(40) J. A. Schellman, *J. Chem. Phys.*, **44**, 55 (1966).

(41) A. I. Smith, U. S. Patent 3187045 (1965); *Chem. Abstr.*, **63**, 9836g (1965).

(42) R. G. Asperger and C. F. Liu, *Inorg. Chem.*, **4**, 1492 (1965).

(43) M. Gullotti, A. Pasini, P. Fantucci, R. Ugo, and R. D. Gillard, *Gazz. Chim. Ital.*, **102**, 855 (1972).

(44) L. Durchleier and K. Ilver, *Dan. Tidsskr. Farm.*, **39**, 264 (1965); *Chem. Abstr.*, **64**, 4238e (1966).

(*R*)-*trans*-*N,N'*-Di(5-bromosalicylidene)-1,2-cyclohexanediamine [(*R*)-10b] was recrystallized from acetone-methanol (85%): yellow needles, mp 186–188°, $[\alpha]^{25}_D - 220^\circ$ (*c* 0.096, CH₃OH, 2-dm).

Anal. Calcd for C₂₀H₂₀Br₂N₂O₂: C, 50.02; H, 4.20. Found: C, 50.06; H, 4.31.

(*R*)-(-)-1,2-Propanediamine [(*R*)-11a]. Technical grade (±)-11a was resolved by a method previously reported.²⁸ After 15 recrystallizations from dilute acetic acid, decomposition of the (+)-tartaric acid salt with sodium hydroxide gave (-)-11a which was extracted into benzene, $[\alpha]^{25}_D - 35^\circ$ (*c* 0.97, C₆H₆, 2-dm) [lit.²⁸ $[\alpha]_D - 34.8^\circ \pm 0.4^\circ$ (C₆H₆)]. The concentration of (-)-11a in benzene was determined by titration with 0.101 *N* hydrochloric acid as outlined above for (-)-10a.

(*R*)-*N,N'*-Di(5-bromosalicylidene)-1,2-propanediamine [(*R*)-11b] was recrystallized from acetone (61%): yellow needles, mp 119–121°, $[\alpha]^{25}_D - 110^\circ$ (*c* 0.23, CH₃OH, 2-dm) (lit.⁴⁶ mp 119°).

Anal. Calcd for C₁₇H₁₆Br₂N₂O₂: C, 46.39; H, 3.66. Found: C, 46.32; H, 3.69.

(*R*)-*N,N'*-Disalicylidene-1,2-propanediamine [(*R*)-11c] was recrystallized from methanol (47%): yellow needles, mp 54–56°, $[\alpha]^{25}_D - 339^\circ$ (*c* 0.49, CH₃OH) [lit. mp 89°⁴³ and 62–63°⁴⁵].

(45) A. P. Terent'ev, G. V. Panova, and E. G. Rukhadze, *Zh. Obshch. Khim.*, **34**, 3013 (1964); *J. Gen. Chem. USSR*, **34**, 3049 (1964).

Anal. Calcd for C₁₇H₁₆N₂O₂: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.46; H, 6.43; N, 9.83.

(*S*)-*N*-(5-Bromosalicylidene)- α -(*p*-nitrobenzyl)ethylamine [(*S*)-21], prepared from (*S*)-(+)- α -(*p*-nitrobenzyl)ethylamine hydrochloride⁴⁶ [mp 194–195°, $[\alpha]^{25}_D + 21^\circ$ (*c* 1.22, H₂O)], was recrystallized from acetone-methanol (76%): yellow needles, mp 115–116°, $[\alpha]^{25}_D + 180^\circ$ (*c* 1.01, absolute C₂H₅OH).

Anal. Calcd for C₁₆H₁₅BrN₂O₃: C, 52.91; H, 4.16. Found: C, 52.93; H, 4.13.

(*S*)-*N,N'*-Di(5-bromosalicylidene)- α -(*p*-aminobenzyl)ethylamine [(*S*)-22], prepared from (*S*)-(+)- α -(*p*-aminobenzyl)ethylamine dihydrochloride⁴⁷ [mp 270° dec, $[\alpha]^{25}_D + 16^\circ$ (*c* 1.23, H₂O)], was recrystallized from methylene chloride-acetone (81%): yellow needles, mp 163–164°, $[\alpha]^{25}_D + 200^\circ$ (*c* 0.20, absolute C₂H₅OH).

Anal. Calcd for C₂₃H₂₀Br₂N₂O₂: C, 53.51; H, 3.91. Found: C, 53.44; H, 3.43.

Methyl *N*-salicylidene-L-tyrosinate [L-23] was recrystallized from methyl acetate: mp 166–167°, $[\alpha]^{22}_D - 268^\circ$ (*c* 2.07, CH₃OH) [lit.⁹ mp 166–167°, $[\alpha]^{22}_D - 270^\circ$ (*c* 2.0, CH₃OH)].

(46) W. Gruber and I. C. Gunsalus, *J. Org. Chem.*, **21**, 1024 (1956).

(47) G. F. Holland, C. J. Buck, and A. Weissman, *J. Med. Chem.*, **6**, 519 (1963).

Tetraalkylhydrazine Radical Cations. The Effect of Alkyl Structure upon Geometry

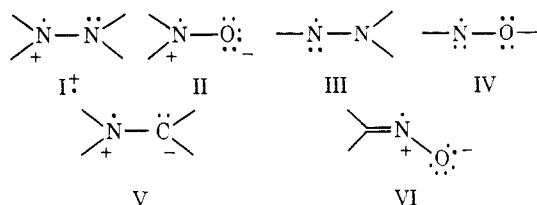
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Contribution from the Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706. Received September 10, 1973

Abstract: The esr spectra of 25 tetraalkylhydrazine radical cations are reported; $a(N)$ varied from 11.9 to 18.8 G depending upon the structure of the alkyl groups present. The effect of temperature upon the esr spectra was investigated for representative compounds. All showed anisotropic broadening of the $\bar{M}_N \neq 0$ lines at low temperatures. For the bridgehead diazabicyclo[3.3.0] and -[4.4.0] systems (19–20⁺ and 11⁺, respectively), the splittings for the eight equivalent β hydrogens observed at room temperature showed an alternating line-width effect as the temperature was lowered, and at low temperatures two sets of four equivalent hydrogens were observed. Estimated ΔG^\ddagger values for the interconversion process (interpreted as double nitrogen inversion) were about 3.4 and 4.5 kcal/mol, respectively. The nitrogen splitting increased as the temperature was lowered for three compounds with larger $a(N)$ splittings, but decreased for tetraethylhydrazine cation (4⁺). INDO calculations on N₂H₄⁺ suggest that hydrazine cation radicals deviate from planarity toward the eclipsed conformation (1c⁺), and indicate β values of 14–37° for the series of compounds investigated. Acceptance of these β values requires accepting that N₂H₄⁺ itself has a β value of about 11° in solution; if it is actually planar, the β values indicated above must be decreased.

Hydrazine radical cations (I⁺) may be formally considered to be members of a class of radicals containing a nitrogen bearing an odd electron which is adjacent to an atom bearing a lone pair of electrons. Other members of this class of radicals include the neutral species dialkyl nitroxides (II),² hydrazyls (III),³ alkoxyamino radicals (IV),⁴ and α -amino carbon radicals

(V);⁵ other resonance forms can obviously be drawn for I–V. All of I–V show the relatively low $a(N)$ (nitrogen esr splitting) one would expect for a π system containing three electrons (one of which must be “anti-bonding”), which we will refer to as “three-electron π bond.” In contrast, iminoxy radicals (VI) have larger



$a(N)$ values, demonstrating an unmistakable degree of σ hybridization in the spin-bearing orbital on nitrogen.⁶

(1) Undergraduate research participant.

(2) For reviews, see (a) A. R. Forrester, J. M. Hay, and R. H. Thomson, “Organic Chemistry of Stable Free Radicals,” Academic Press, New York, N. Y., 1968, pp 180–246; (b) S. F. Nelsen in “Free Radicals,” Vol. II, J. K. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, pp 539–556.

(3) (a) For a review of aryl derivatives, see ref 2a, pp 137–179; (b) D. E. Wood, C. A. Wood, and W. A. Lathan, *J. Amer. Chem. Soc.*, **94**, 9278 (1972); (c) R. Fantechi and G. A. Helcké, *J. Chem. Soc., Faraday Trans. 2*, **68**, 924 (1972); (d) V. Malatesta and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6110 (1973); (e) S. F. Nelsen and R. T. Landis, *ibid.*, **95**, 2719 (1973).

(4) W. C. Danen and C. T. West, *J. Amer. Chem. Soc.*, **93**, 5582 (1971).

(5) D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, **52**, 3840 (1970).

(6) For leading references, see ref 2b, p 562.