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Application of the Salicylidenimino Chirality Rule to Chiral 1-Alkyl-2-propynylamines and 1-Alkyl-2-propenylamines[1]

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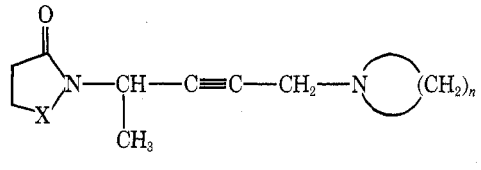
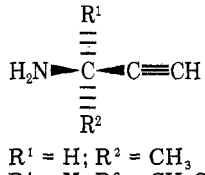
The sign of the Cotton effects near 255 and 315 nm in the circular dichroism (CD) spectra of the *N*-salicylidene derivatives of chiral 1-alkyl-2-propynylamines and 1-alkyl-2-propenylamines correlates with their absolute configurations. The Cotton effects are generated by the coupled oscillator mechanism and their sign is the same as the chirality (right-handed screw for positive chirality) of the triple and the double bond with the phenyl group–methine bond of the salicylidenimino chromophore. The chirality is determined by both the absolute configuration and the preferred conformation of the respective *N*-salicylidene derivatives. Thus those derivatives with the *R* configuration display negative Cotton effects near 255 and 315 nm, and those with the *S* configuration, positive.

In connection with the study of the stereospecific blockade of the motor effects of the muscarinic agent oxotremorine, *N*-(4-pyrrolidino-2-butynyl)-2-pyrrolidone, by *N*-(4-*tert*-amino-1-methyl-2-butynyl)-substituted succinimides (1) and 2-pyrrolidones (**2**),[3] the respective enantiomers of 1 and **2** were

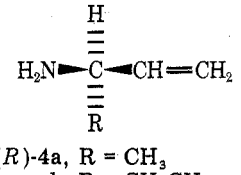


1a, X = CO; *n* = 4
b, X = CO; *n* = 6
2, X = CH_2; *n* = 4

prepared from the enantiomers of 1-methyl-2-propynylamine (**3a**),[3] the absolute configurations of the latter being rigorously

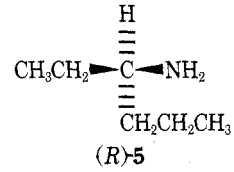


(*R*)-**3a**, R^1 = H; R^2 = CH_3
b, R^1 = H; R^2 = CH_3CH_2
c, R^1 = H; R^2 = $CH_3CH_2CH_2$
d, R^1 = CH_3; R^2 = CH_3CH_2



(*R*)-**4a**, R = CH_3
b, R = CH_3CH_2
c, R = $CH_3CH_2CH_2$

established in two ways.[3,4] For the possible synthesis of chiral analogues of **1** and **2**, the enantiomers of 1-ethyl-2-propynylamine (**3b**), 1-propyl-2-propynylamine (**3c**) and 1-ethyl-1-methyl-2-propynylamine (**3d**) were also prepared and their absolute configurations were also established by chemical transformations.[5,6] Partial reduction of (*R*)-**3a** and of the enantiomers of **3b** and **3c** with hydrogen over Lindlar's catalyst afforded (*R*)-1-methyl-2-propenylamine [(*R*)-**4a**] and the enantiomers of 1-ethyl-2-propenylamine (**4b**) and 1-propyl-2-propenylamine (**4c**).[7] Reduction of (*S*)-**3c** with hydrogen over Raney nickel gave (*R*)-1-ethylbutylamine [(*R*)-**5**].[7] Thus a group of chiral 1-alkyl-2-propynylamines (**3**) and 1-alkyl-2-propenylamines (**4**) of established configuration became available for a rigorous test of the salicylidenimino chirality rule[8] for the deduction of the absolute configurations of amines of this type.

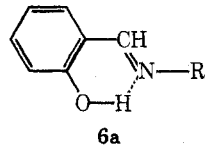


(*R*)-**5**

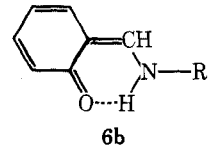
We now report the preparation of the *N*-salicylidene derivatives (**6**) of an enantiomer of each of these amines and the interpretation of the circular dichroism (CD) spectra of these derivatives.

Results and Discussion

Electronic Absorption Spectra. The electronic (isotropic) absorption (EA) spectra of the *N*-salicylidene derivatives of the 1-alkyl-2-propynylamines (**3**), of the 1-alkyl-2-propenylamines (**4**), and of 1-ethylbutylamine (**5**) in hexane exhibit three absorption bands with maxima at 318–320 (log ε 3.69–3.71), 254–255 (log ε 4.11–4.15), and 216 nm (log ε 4.40–4.42), designated as bands I, II, and III, respectively. These bands are assigned to transitions of the intramolecularly hydrogen-bonded salicylidenimino chromophore (**6a**).[8]



6a



6b

As is frequently the case,[9] band II also shows a shoulder at 260–261 nm (log ε 4.07–4.09) and at a slightly longer wavelength than the absorption maximum. In methanol, a broad band with maximum at 400–403 nm (log ε 2.03–2.19 for the derivatives of **3a–3d**, 2.97–2.99 for those of **4a–4c**, and 3.23 for that of **5**) becomes evident, and bands I, II, and III show a slight decrease in intensity. A shoulder near 260 nm is no

Table I. Circular Dichroism Data for the *N*-Salicylidene Derivatives of Some Chiral Amines

Registry no.	Amine	Solvent	CD max, λ, nm ([θ][a]) Quinoid	I		II	III
54139-78-5	(*R*)-**3a**	Hexane		322 (−4400)	268 (+3700)	250 (−4 300)	220 (+9 000)
		MeOH	400 (−120)[b]	316 (−4900)	269 (+6100)	251 (−5 900)	219 (+7 800)
50285-35-3	(*S*)-**3b**	Hexane		319 (+5700)	267 (−4100)	251 (+4 700)	220 (−11 000)
		MeOH	400 (+130)[b]	316 (+5600)	268 (−6800)	250 (+6 500)	221 (−11 000)
62227-54-7	(*S*)-**3c**	Hexane		318 (+6200)	268 (−4000)	250 (+5 400)	221 (−13 000)
		MeOH	400 (+140)[b]	317 (+5400)	271 (−7000)	252 (+5 900)	219 (−11 000)
62141-59-7	(*R*)-**3d**	Hexane		320 (−2700)		255 (−4 300)	224 (+3 200)
		MeOH	400 (−60)[b]	316 (−3000)		254 (−4 9000)	221 (+2 500)
63731-07-7	(*R*)-**4a**	Hexane		320 (−8200)	272 (+4200)	255 (−17 000)	213 (−14 000)
		MeOH	400 (−790)	316 (−6000)	271 (+3500)	251 (−15 000)	210 (−9 400)
63731-08-8	(*R*)-**4b**	Hexane		320 (−7300)	272 (+5900)	254 (−19 000)	214 (−15 000)
		MeOH	400 (−800)	316 (−5300)	272 (+5300)	252 (−16 000)	212 (−11 000)
63731-09-9	(*S*)-**4c**	Hexane		320 (+5100)	272 (−7200)	254 (+16 000)	214 (+15 000)
		MeOH	400 (+580)	315 (+3900)	272 (−5800)	251 (+14 000)	213 (+11 000)
63731-10-2	(*R*)-**5**	Hexane		320 (−2400)		255 (−2 400)	224 (+3 000)
		MeOH	400 (−590)	316 (−1800)		252 (−2 000)	220 (+2 400)

[a] Molecular ellipticity. [b] Shoulder.

longer evident in any of the spectra, but the derivatives of **3–5** now show a shoulder at 277–278 nm (log ε 3.43–3.61). The absorption bands at 400 and 278 nm are assigned to a quinoid tautomer (**6b**), stabilized by and in greater concentration in the more polar solvent.[10,11]

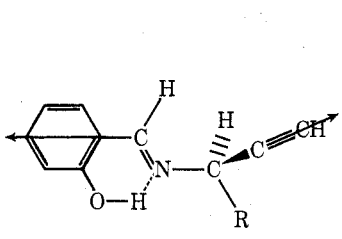
Circular Dichroism Spectra. The *N*-salicylidene derivatives show circular dichroism (CD) spectra with multiple Cotton effects (Table I) which in general correspond to the EA maxima and which are generated by the coupled oscillator mechanism.[12] Thus in the ethynyl (**3**) and ethenyl (**4**) derivatives, the dominant contribution to the circular dichroism arises from the interaction of the salicylidenimino chromophore with the lowest energy $\pi \rightarrow \pi^*$ transition of the ethynyl ($^1A_{1\mu} \leftarrow {}^1A_{1g}$ of acetylene at ca. 152 nm[13]) and the ethenyl group [$^1B_{1\mu} \leftarrow {}^1A_{1g}$ (N-V) of ethylene at ca. 175 nm[13]], both red-shifted by alkyl substitution.

The assignment of the Cotton effects near 400, 320, 252, and 220 nm as shown in Table I is straightforward, but that for the 270-nm Cotton effect is somewhat more difficult. The latter cannot be attributed to an electronic transition of the quinoid tautomer since it is observed in hexane. Since a carbon–carbon triple bond has no electronic transition in this spectral region and a carbon–carbon double bond has only a weak singlet → triplet transition above 200 nm,[13] the CD maximum near 270 nm in the *N*-salicylidene derivatives of **3a–3c** and **4a–4c** must be assigned to some transition of the salicylidenimino chromophore. One possibility is a weak $n \rightarrow \pi^*$ transition of the azomethine group, similar to that at 240 nm in nonconjugated azomethines[14] but shifted to longer wavelength by conjugation with the phenyl ring. Another is a weak $\pi \rightarrow \pi^*$ transition of the intramolecularly hydrogen-bonded salicylidenimino chromophore. Dynamic coupling of this transition with the ethynyl and ethenyl transitions results in a large enhancement of the CD band near 270 nm.

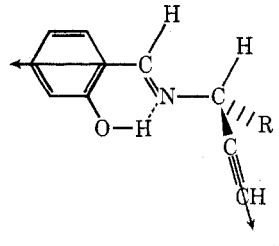
A similar CD maximum near 270 nm, opposite in sign to band I, was found in the spectra of a number of the *N*-salicylidene derivatives of α- and β-arylalkylamines,[1,8,15–18] acyclic β-hydroxyalkylamines,[19] steroidal amines,[20] and α-amino acids and esters.[1] In most of these spectra, band II had the same sign as band I and was easily identified. Since the 270-nm band was observed for the α-(1-naphthyl)- and α-phenylalkylamine derivatives in nonpolar solvents, it was assigned to the aryl group of the amine moiety, both the naphthyl and phenyl groups showing absorption bands near 270 nm.[8,15] For the α- and β-(2-thienyl)alkylamine and β-hydroxyalkylamine derivatives, also showing the CD maximum near 270 nm in hexane, the band was unassigned.[1,19] In the spectra of some of the steroidal amine derivatives and the α-amino acid derivatives, examined only in polar solvents, the maximum was assigned to the quinoid tautomer.[1,21] For a few other steroidal amine and the α-amino ester derivatives, the band was assigned to band II of the hydrogen bonded salicylidenimino chromophore.[1,21] Some of these earlier assignments of this band may require revision in view of the present results.

Since the CD maxima associated with bands I and II in the *N*-salicylidene-1-alkyl-2-propynylamines and *N*-salicylidene-1-alkyl-2-propenylamines are easily identified, the sign of these maxima can be correlated with the absolute configurations of the respective amines, much the same as is done for *N*-salicylidene derivatives of chiral α- and β-arylalkyl amines[1,8,15–18] and α-amino acids.[1] In propynes and propenes, the electric transition moment of the lowest energy $\pi \rightarrow \pi^*$ transition is directed along the multiple bond.[13] The transition moments of bands I and II in the salicylidenimino chromophore are approximately aligned with the phenyl group–methine carbon bond.[8] Thus the sign of the circular dichroism associated with bands I (315 nm) and II (255 nm) in the *N*-salicylidene derivatives of **3** and **4** should be the same as the chirality of the triple and double bond with the phenyl group–methine bond.[8] This chirality is determined by both the absolute configuration and the preferred conformation of the respective derivatives.

For the intramolecularly hydrogen-bonded (*R*)-*N*-salicylidene-1-alkyl-2-propynylamines [(*R*)-**7**], the proton magnetic resonance (^1H NMR) spectra (Table II) in which the methine proton of the salicylidenimino group is seen as a doublet (J = 1.6 Hz) suggest a perferred conformation depicted as (*R*)-**7a**.[22] This conformation is somewhat different from an al-



(*R*)-**7a**



(*R*)-**7b**

ternate one [(*R*)-**7b**] analogous to that deduced for an *N*-salicylidene-α-phenylalkylamine[8] in which the hydrogen atom

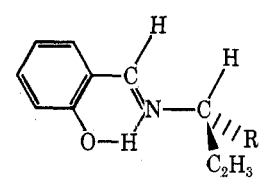
Table II. Proton Magnetic Resonance Data for the *N*-Salicylidene Derivatives of Some Chiral Amines

Amine	Solvent	δ,[a] ppm (*J*,[b] Hz) N=C*H*[c]	N—C*H*[d]
(*R*)-**3a**	CCl_4	8.61 (1.6)	4.51
	CD_3OD	8.65 (1.5)	4.50
(*S*)-**3b**	CCl_4	8.62 (1.6)	4.40
(*S*)-**3c**	CCl_4	8.62 (1.6)	4.48
(*R*)-**3d**	CCl_4	8.68	
(*R*)-**4a**	CCl_4	8.30	3.89
	CD_3OD	8.40	3.94
(*R*)-**4b**	CCl_4	8.30	3.60
(*S*)-**4c**	CCl_4	8.30	3.72
(*R*)-**5**	CCl_4	8.23	2.97
	CD_3OD	8.36	3.10

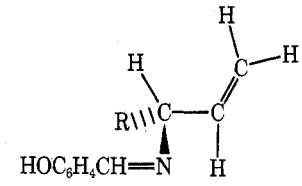
[a] Chemical shift downfield from Me_4Si = 0. [b] Coupling constant. [c] Doublet or if no coupling constant given, singlet. [d] Multiplet.

at the chiral center eclipses the carbon–nitrogen double bond of the salicylidenimino group. The chirality of the relevant bonds as shown in both (*R*)-**7a** and (*R*)-**7b**, however, is negative, and the *N*-salicylidene derivative of (*R*)-**3a** shows negative Cotton effects for bands I and II. Derivatives of those amines [(*S*)-**3b** and (*S*)-**3c**] with the enantiomeric configuration give rise to positive Cotton effects. Since an ethyl group is larger in effective bulk size than a methyl group, the *N*-salicylidene derivative of (*R*)-**3d** should have a preferred conformation analogous to (*R*)-**7a** or (*R*)-**7b**, the methyl and ethyl groups replacing the hydrogen atom and the R group, respectively, with negative chirality for the coupled oscillators. Thus negative Cotton effects for bands I and II are observed. The reduced molecular ellipticity for these maxima can be explained on the basis of a reduced preference for the conformer of lowest energy since a methyl group is more nearly the same size as an ethyl group than is a hydrogen atom compared to a methyl group. The absence of a 270-nm CD maximum in the spectrum of the derivative of (*R*)-**3d** may also be a consequence of this same reduced preference for the conformer of lowest energy.

In the ^1H NMR spectra of the intramolecularly hydrogen-bonded (*R*)-*N*-salicylidene-1-alkyl-2-propenylamines [(*R*)-**8**], the methine proton of the salicylidenimino group appears as a singlet, indicating a preferred conformation [(*R*)-**8a** and (*R*)-**8b**] such that the hydrogen atom at the chiral center is eclipsed by both the carbon–nitrogen [(*R*)-**8a**] and carbon–carbon double bonds [(*R*)-**8b**].[22] For this conformation, the chirality of the relevant transition moments is negative and negative Cotton effects are observed for the derivatives of



(*R*)-**8a**



(*R*)-**8b**

(*R*)-**4a** and (*R*)-**4b**. Positive Cotton effects are observed for the derivative of (*S*)-**4c**.

In both the ethynyl and ethenyl derivatives the sign of the Cotton effects associated with band III may be understood if this band is the bathochromically shifted ^1B benzenoid transition.[23] Thus there are two electric transition moments, one approximately parallel and the other perpendicular to the methine carbon–phenyl group bond. Both transitions give Cotton effects with opposite signs resulting in partial cancellation. This may explain the observation that the intensity of band III is not much greater than and is sometimes less than the intensity of band II. The opposite signs for bands II and III for the 1-alkyl-2-propynylamine (**3**) derivatives indicate that in their preferred conformation the orientation of the interacting chromophores is such that the perpendicular component of the ^1B transition dominates. On the other hand, with the 1-alkyl-2-propenylamine (**4**) derivatives, the parallel component of the ^1B transition, apparently at a shorter wavelength than the perpendicular one, wins out, and these derivatives show Cotton effects for bands II and III of the same sign.

The negative Cotton effects for bands I and II of the *N*-salicylidene derivative of (*R*)-1-ethylbutylamine [(*R*)-**5**] are also most likely generated by a coupled oscillator mechanism,[12,24] but because of the many conformational possibilities for (*R*)-**5**, no simple prediction concerning the sign of the observed Cotton effects is possible. It is to be noted, however, that (*S*)-*N*-salicylidene-*sec*-butylamine displays positive Cotton effects, near 315 and 255 nm, while those of (*R*)-*N*-salicylidene-2,2-dimethyl-3-aminobutane are negative, and neither shows a CD maximum near 270 nm.[19]

Experimental Section

Optical rotations at the sodium D line were measured in a 1-dm tube with a Perkin-Elmer 141 spectropolarimeter. Electronic (isotropic) absorption (EA) spectra were obtained with a Zeiss Spektralfotomer Pm QII. Circular dichroism (CD) spectra were recorded on a Jasco J-41 spectropolarimeter at 20 °C with a cell length of 2 mm. Proton magnetic resonance (^1H NMR) spectra were recorded with a Perkin-Elmer R 12 B spectrometer at 37 °C. Elemental analyses were done at the Microanalytical Laboratory, Royal Agricultural College, Uppsala, Sweden.

Table III. *N*-Salicylidene Derivatives of Chiral Amines

		N-Salicylidene derivative				Elemental analysis					
						Calcd			Found		
Registry no.	Amine	Bp, °C (mmHg)	Yield, %	$n^{22}D$	$[\alpha]^{22}D$, deg (*c* EtOH)	C	H	N	C	H	N
63731-13-5	(*R*)-**3a**	80 (0.3)	70	1.5682	+14 (1.2)	76.27	6.40	8.09	75.11	6.28	8.06
63731-14-6	(*S*)-**3b**	105 (0.6)	86	1.5614	+8 (1.3)	76.98	7.00	7.48	76.88	6.94	7.56
63731-15-7	(*S*)-**3c**	112 (0.6)	88	1.5534	+5 (1.5)	77.58	7.51	6.96	77.36	7.55	6.91
63731-16-8	(*R*)-**3d**	105 (0.6)	90	1.5480	−66 (1.2)	77.58	7.51	6.96	76.92	7.60	7.10
63731-17-9	(*R*)-**4a**	90 (0.5)	72	1.5575	−170 (1.4)	75.40	7.48	7.99	75.28	7.52	7.83
63731-18-0	(*R*)-**4b**	95 (0.7)	74	1.5513	−154 (1.4)	76.16	7.99	7.40	76.31	8.07	7.34
63731-19-1	(*S*)-**4c**	100 (0.5)	84	1.5450	+111 (1.3)	76.81	8.43	6.89	76.70	8.47	6.80
63765-60-6	(*R*)-**5**	95 (0.5)	86	1.5338	−37 (1.2)	76.06	9.33	6.82	75.94	9.18	6.85

***N*-Salicylidene derivatives** were prepared from the respective amines[4-7] by the usual procedure.[25] Yields and physical properties are given in Table III.

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Heterogeneous Catalysis by Solid Superacids. 3.[1a] Alkylation of Benzene and Transalkylation of Alkylbenzenes over Graphite-Intercalated Lewis Acid Halide and Perfluorinated Resin-Sulfonic Acid (Nafion-H) Catalysts

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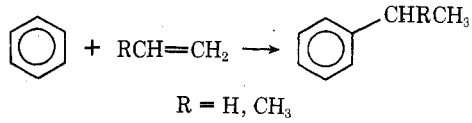
The use of superacidic solid catalysts in heterogeneous gas-phase alkylation reactions, such as the ethylation of benzene by ethene and the transethylation of benzene with diethylbenzene, was studied. Such catalysts enable us to conduct the reactions under relatively mild conditions and to obtain clean reaction products. Reactions were carried out in a flow system, in the gas phase, in the temperature range of 125–210 °C at atmospheric pressure. Intercalated $AlCl_3$ and $AlBr_3$ gave good initial yields of alkylated products. The lifetime of the catalyst was, however, limited as the active Lewis acid is leached out from the catalyst, causing a sharp decline in the catalytic activity with on-stream time. Other possible reasons of the deactivation of the catalyst are also discussed. A perfluorinated sulfonic acid resin catalyst (Nafion-H) was found to have a much better stability, while showing good catalytic activity. Alcohols were also found to dehydrate in the gas phase efficiently over this catalyst and could be used as alkylating agents for benzene.

Friedel–Crafts alkylation and transalkylation reactions are traditionally carried out in the liquid phase. Catalysts are generally based on aluminum chloride and related Lewis acid halides. The ethylation of benzene with ethylene to form ethylbenzene using aluminum chloride as catalyst is one of the largest chemical processes carried out in industry. Application of solid supported catalysts in heterogeneous vapor phase ethylation started to gain importance only recently. One of the major difficulties is the sluggishness of the ethylation reaction. Ethene is far less readily protonated than, for example, the more polar propene, and its equilibrium with the ethyl cation is rather unfavorable. Few (if any) of the known solid acid catalysts are able to catalyze efficiently the ethylation of benzene or the transethylating benzene with polyethylbenzenes (which are inevitably formed as by-products in the ethylation of benzene). This is not the case with the isopropylation of benzene to cumene. Cumene has been industrially produced for decades over supported acid catalysts such as supported phosphoric acid. Obviously, the more polar propene is protonated much more readily than ethene and polyisopropylbenzenes also transalkylate benzene with greater ease.

In continuation of our studies of Friedel–Crafts and superacid chemistry, our interest was directed to the possibility of applying solid superacidic catalysts to heterogeneous reactions.[1-3] These catalysts can be based either on Lewis acid halides bound or intercalated to suitable supports or solid (polymeric) protic acid, such as perfluorinated resin sulfonic acids.

Results and Discussion

The alkylation of benzene with ethene and propene (eq 1)



(1)

R = H, CH_3

and the transethylation of benzene with diethylbenzenes (eq 2) was studied over several solid superacidic catalysts. Reac-

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