Experimental Section

Melting points were determined with a Mel-Temp apparatus and are uncorrected. It was difficult to obtain NMR spectra of the bispyrans because of their low solubility. The mass spectra were determined for all compounds and show a characteristic large peak for M^+ (relative intensity 100%) and M^{2+} (relative intensity 20–40%), but all other peaks are less than 1%. The mass spectra were obtained on an AEI MS-30 mass spectrometer, absorption spectra on a Cary-17 spectrometer, and IR spectra on a Beckman IR 4200 spectrometer.

4,4′-(1,2-Ethanediylidene)-2,2′,6,6′-tetraphenylbis(4*H*-pyran) (4). A suspension of 1.95 g (5.9 mmol) of 2,6-diphenylpyrylium perchlorate in 50 mL of dry tetrahydrofuran was stirred under argon and cooled in a dry ice–acetone bath. A 1.1 M solution (5.4 mL, 5.9 mmol) of sodium diethylphosphonate[7] was added by syringe, and the stirring was continued until a clear solution was obtained (about 10 min). To this solution was added 2.4 mL (5.9 mmol) of 2.5 M butyllithium and after 5 min 1.63 g (5.9 mmol) of 2,6-diphenyl-4-(formylmethylene)-4*H*-pyran. The reaction mixture was stirred for 1 h at −78 °C, allowed to stand overnight at room temperature, and then evaporated to dryness. The residue was dissolved in methylene chloride and passed through a column of Florisil (eluted with methylene chloride). The eluant was evaporated to dryness, and the residue was recrystallized twice from toluene: IR (KBr) 1659, 1625, 1601, 1581, 1495, 1451, 1345, 1288, 1244 cm^{-1}; mass spectrum, *m/e* 490, 385, 245, 105, 77; absorption spectrum (CH_2Cl_2) 478 (6.43×10^4), 280 (2.4×10^4), 256 nm (2.5×10^4).

The other ethanediylidene dimers in Table I were prepared in the same manner from the appropriate starting materials. The spectral properties of these compounds are collected in Table II (see supplementary material).

Compound **12** was prepared by the method described for **4** from 2,6-diphenylpyrylium perchlorate (12 mmol) and 2-(formylmethylene)-1-methylbenzothiazolene (12 mmol), giving 0.83 g (17%) of **12**, mp 227–228 °C.

Anal. Calcd for $C_{27}H_{21}NOS$: C, 79.6; H, 5.2; N, 3.4. Found: C, 79.3; H, 5.0; N, 3.3.

Registry No. 2 (X = O), 75548-91-3; **2** (X = S), 75548-92-4; **3** ($R_1 = R_2 = Ph$; $R_3 = R_4 = H$; Y = O), 20399-89-7; **3** ($R_1 = R_2 = Ph$; $R_3 = R_4 = H$; Y = S), 75548-93-5; **3** (R_1R_3 = benzo; R_2R_4 = benzo; Y = S), 56389-52-7; **3** (R_1R_3 = 1,2-naptho; R_2R_4 = 1,2-naptho; Y = O), 75548-94-6; **3** ($R_1 = Ph$; $R_3 = H$; R_2R_4 = benzo; Y = S), 20399-91-1; **4** ($R_1 = R_2 = Ph$; $R_3 = R_4 = H$; X = O; Y = O), 62041-62-7; **5** ($R_1 = R_2 = Ph$; $R_3 = R_4 = H$; X = S; Y = S), 51829-03-9; **6** ($R_1 = R_2 = Ph$; $R_3 = R_4 = H$; X = O; Y= S), 75548-95-7; **7** (R_1R_3 = benzo; R_2R_4 = benzo; X = O; Y = S), 75548-96-8; **8** (R_1R_3 = 1,2-naptho; R_2R_4 = 1,2-naptho; X = O; Y = O), 75548-97-9; **9** ($R_1 = Ph$; $R_3 = H$; R_2R_4 = benzo; X = O, Y = S), 75548-98-0; **11**, 4616-17-5; **12**, 75558-43-9.

Supplementary Material Available: Spectral data for compounds **5**–**9** and **12** (2 pages). Ordering information is given on any current masthead page.

(7) Commercially available from Organometallics, Inc., East Hampstead, NH.

Optically Active Amines. 29.[1] Application of the Salicylidenimino Chirality Rule to Amino Sugars

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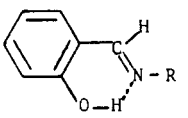
Some time ago, Inouye[3–5] prepared the *N*-salicylidene derivatives of some amino sugars and reported the optical rotatory dispersion (ORD) and circular dichroism (CD) spectra of these derivatives. He suggested the use of such spectra for the determination of the configuration of the amino group in monosaccharides[3,4] and as a means of identification of amino oligosaccharide antibiotics.[5]

In methanol, the *N*-salicylidene derivatives of monosaccharides generally show Cotton effects (CEs) of the same sign near 405, 315, and 255 nm. The latter two are assigned to $\pi \rightarrow \pi^*$ electronic transitions of the hydrogen-bonded salicylidenimino (SI) group (**1**) and that near



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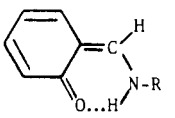

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405 nm to a transition of the quinoid tautomer **2**.[6,7] In dioxane, the proportion of the quinoid tautomer is reduced in the less polar solvent,[7] and the 405-nm CE is weak and is usually not observed while those near 315 and 255 nm have enhanced intensities.

Inouye concluded that for D-glucose derivatives, positive CEs are correlated with the D (*S*) configuration of the 2-SI group and negative CEs with the L (*R*) configuration of the 1- and 3-SI groups.[3] Extension of the correlation to mannose derivatives was less successful.[3]

We now note, however, that the salicylidenimino chirality rule[8] can be used to correlate the sign of the observed CEs near 315 and 255 nm with the absolute configuration of many amino monosaccharides (Table I), much the same as can be done for similar derivatives of terpene[9] and steroidal amines.[10] The rule is based on the model that the 315- and 255-nm CEs originate from interaction of the respective transition moments of the hydrogen-bonded SI chromophore with bond transition moments in the rest of the molecule. The sign of a contribution to the CEs by a given bond usually can be determined from the chirality that the bond has with the attachment bond of the SI group, a positive contribution for positive chirality (right-handed screw) and negative for negative chirality (left-handed screw).[8] In cases where these two bonds are coplanar, the chirality that the bond has with transition moments of the SI chromophore, the moments situated at the center of the benzene ring with long axis polarization, is used. The contribution of a C–H bond is neglected, and that of a C–C bond outweighs that of a C–O bond.[11,12] When a C–C or C–O bond is vicinal to the SI attachment bond, its contribution predominates unless cancellation occurs. The preferred chair conformation of the tetrahydropyran ring of a hexose makes the ring bond contributions for an equatorial or axial 3-SI group negligible due to complete mutual cancellation as a result of symmetry.

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Table I. Predicted and Observed Cotton Effects in the Circular Dichroism Spectra of the *N*-Salicylidene Derivatives of Amino Sugars in Methanol

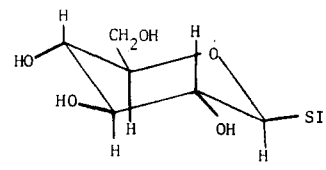
compd	amino sugar	anomer (SI group)	bond (chirality) with the SI group transition moments: vicinal	homovicinal	Cotton effects near 315 and 255 nm[a]: predicted	obsd
3	β-D-glucopyranosylamine		C(2)-O (−)		−	−
4	β-D-mannopyranosylamine		C(2)-O (+)		+	+
5	methyl 2-amino-2-deoxy-α-D-glucopyranoside		C(1)-O (+), C(3)-O (+)		+	+[b]
6	methyl 3-amino-3-deoxy-α-D-mannopyranoside		C(2)-O (−), C(4)-O (−)		−	−[c]
7	methyl 2-amino-2-deoxy-β-D-glucopyranoside		C(1)-O (−), C(3)-O (+)	C(4)-O (+)	+	+
8	methyl 3-amino-3-deoxy-α-D-glucopyranoside		C(2)-O (+), C(4)-O (−)	C(1)-O (+), C(5)-C(6) (−)	−[d]	−[d]
9	methyl 3-amino-3-deoxy-β-L-glucopyranoside		C(2)-O (−), C(4)-O (+)	C(1)-O (−), C(5)-C(6) (+)	+[d]	*e*
10	2-amino-2-deoxy-D-glucose	β[f]	C(1)-O (−), C(3)-O (+)	C(4)-O (+)	+	+
		α	C(1)-O (+), C(3)-O (+)			
11	2-amino-2-deoxy-D-galactose	β[f]	C(1)-O (−), C(3)-O (+)	C(4)-O (+)	+	+
		α	C(1)-O (+), C(3)-O (+)			
12	2-amino-2-deoxy-D-mannose	β[f]	C(1)-O (+), C(1)-O[h] (−), C(3)-C(4) (+), C(3)-O (−)		*g*	*e*
		α	C(1)-O (±0), C(1)-O[h] (−), C(3)-C(4) (+), C(3)-O (−)			
13	methyl 6-amino-6-deoxy-α-D-glucopyranoside		C(5)-O (+), C(5)-C(4) (−)[j]		*g*	+[b,d]
14	methyl 3,6-diamino-3,6-dideoxy-α-D-mannopyranoside	(C-6)	C(5)-O (+),[i] C(5)-C(4) (−)[j]		−	−
		(C-3)	C(2)-O (−), C(4)-O (−)			
15	methyl 3,6-diamino-3,6-dideoxy-α-D-glucopyranoside	(C-6)	C(5)-O (+),[i] C(5)-C(4) (−)[j]		*g*	+
		(C-3)	C(2)-O (+), C(4)-O (−)	C(1)-O (+), C(5)-C(6) (−)		
16	methyl 3,6-diamino-3,6-dideoxy-α-D-altropyranoside		*k*		*g*	*l*
17	5-amino-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose		C(4)-O (+),[m] C(4)-C(3) (−)		+[d]	+[d]
18	3-*O*-benzyl-6-*O*-(triphenylmethyl)-1,2-*O*-isopropylidene-5-amino-5-deoxy-α-D-glucofuranose				*g*	+[n]
19	3-*O*-benzyl-6-*O*-(triphenylmethyl)-1,2-*O*-isopropylidene-5-amino-5-deoxy-β-L-idofuranose				*g*	−[n]
20	2-amino-2-deoxy-D-glucitol				*g*	+

[a] Cotton effects (CEs) reported in ref 3 or as otherwise noted. [b] Sign deduced from ORD curve. [c] Weak in methanol but strong in dioxane. [d] Weak. [e] No CE observed. [f] More stable anomer. [g] No unambiguous prediction. [h] Ring oxygen. [i] Conformer **22a**; see text. [j] Conformer **22b**; see text. [k] Chirality of coupling not predictable. [l] Couplet, $[\Theta]_{267}$ −15 000 and $[\Theta]_{251}$ +23 000, centered at 259 nm. [m] Dominant contribution. [n] As reported in ref 4, only the 315-nm CE was observed.

The contribution due to ring bonds is also negligible for an equatorial 1-, 2-, or 4-SI group since the attachment bond of the SI group and the vicinal ring bonds are anticoplanar.

These considerations taken together with the preferred conformation of the sugar moiety allow a prediction for the sign of the CEs near 315 and 255 nm. As seen in Table I, agreement between prediction and observation is excellent in those cases where prediction is unambiguous.

For compounds **3**–**6**, the CEs arise by interaction of one or two vicinal C–O bonds with an equatorial 1- or 2-SI chromophore, and the sign of the observed CEs agrees with the chiralities that the vicinal C–O bonds have with the attachment bond of the SI group. Thus, the chirality that the C(2)–O bond in *N*-salicylidene-β-D-glucopyranosylamine (**3**) has with the attachment bond of the 1-SI group



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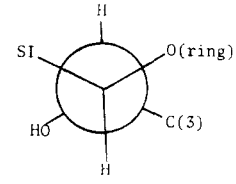

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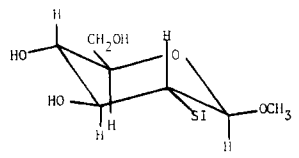
is negative (**21**), and negative CEs near 315 and 255 nm are observed. The observation that **3** and **4**, differing only

in the configuration at C-2, show strong, negative and positive CEs, respectively, is in agreement with the conclusion that any contribution from ring bonds for an equatorial 1-, 2-, or 4-SI group need not be considered.

The mutual cancellation of the vicinal bond contributions in **7–9** necessitates the consideration of homovicinal bonds. These bonds are coplanar with the equatorial 2- or 3-SI group attachment bond and the chiralities that they have with the SI group transition moments are deduced by using the perferred conformation of the SI group about its attachment bond in which the methine hydrogen atom of the salicylidenimino group eclipses the hydrogen atom at the chiral center to which the nitrogen atom is attached.[13] On this basis, methyl 2-(salicylidenimino)-2-deoxy-β-D-glucopyranoside (**7**) is correctly predicted to



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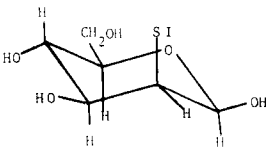
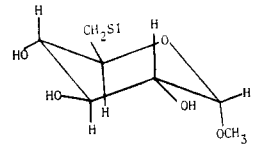


8-12

show positive Cotton effects. For **8** and **9** substantial cancellation of the homovicinal bond contributions occurs, but since the contribution by the C(5)–C(6) bond is greater than that by the C(1)–O bond, the CEs are predicted to be weakly negative and weakly positive, respectively. In agreement with this analysis, the CEs for **8** are weakly negative, and none is observed for **9**.

For **10–12** the presence of α and β anomers must be considered. Both anomers of **10** and **11** are predicted to show positive CEs, and the overall prediction for **10** and **11** is unambiguously positive. The SI group in **12** is preferably in an axial conformation (β-**12**), and the vicinal ring bond contribution must be taken into account. Since the sign of the observed CEs is the algebraic sum of a number of mutually cancelling vicinal C–C and C–O bond contributions present in both anomers, an unambiguous prediction as to the sign of the observed Cotton effects is not possible. That no CE for **12** was observed confirms this assessment.

The SI group in methyl 6-(salicylidenimino)-6-deoxy-α-D-glucopyranoside (**13**) is not attached to the tetra-



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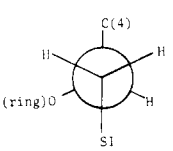
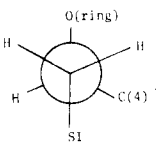


22a



22b

hydropyran ring, and two rotamers of the SI group about the C(6)–C(5) bond, **22a** and **22b** with positive and negative contributions, respectively, must be considered. The experimentally observed weak, positive CEs suggest the greater importance of conformer **22a**. In **14–16**, each with an SI group at C-3 and C-6, the contribution to the CEs of both SI groups must be considered. The equatorial conformation and large separation of the 3-SI and 5-(SImethyl) groups in **14** and **15** is such that coupling between the SI groups[8] should be unimportant, and the contribution from each chromophore can be assessed separately. The contribution from the 3-SI group in **14** is strongly negative (cf. **6**) and is stronger than the weak, positive 6-SI contribution. The CEs for **14** are then unambiguously predicted to be negative. The 3-SI contribution in **15** is weakly negative (cf. **8**), but the weak, positive contribution from the 6-SI group does not allow a prediction of the sign of the CEs. The preferred chair conformation of **16** requires that either the 3-SI group or the 5-(SImethyl) group be in an axial conformation with the possibility of dynamic coupling[8] between the two SI groups. The couplet centered at 259 nm in the spectrum of **16** confirms dynamic coupling, and no prediction as to the chirality of this coupling and hence the sign of the observed Cotton effects is made. The same appears to be true for the *N*-salicylidene derivatives of the amino oligosaccharide antibiotics.[5] The relatively strong CEs in the spectra of these derivatives indicate dynamic coupling among the three or more SI groups, and the conformational mobility of these systems prevents prediction as to the sign of the observed CEs.

Conformation analysis for the preferred conformation of the 5-SI group about the C(4)–C(5) bond in **17**, similar to that for the 6-SI group in **13**, can also be made. On the basis of a preferred conformation similar to **22a**, weak, positive CEs are predicted for **17**.

For the remaining compounds in Table I (**18–20**), the CEs arise by a similar mechanism. Predictions as to signs of the observed CEs are not possible by the summation of bond contributions because of the conformational varients present. It is to be noted, however, that **18** and **19** with epimeric 5-SI groups show essentially enantiomeric CD curves with a positive CE near 315 nm for **18** and a negative CE for **19**.[4]

Acknowledgment. We thank the National Science Foundation for a grant (CHE77-24293) supporting this work.

Registry No. **3**, 19124-27-7; **4**, 19124-28-8; **5**, 19124-32-4; **6**, 19124-36-8; **7**, 19124-33-5; **8**, 19124-34-6; **9**, 19124-35-7; β-**10**, 51471-41-1; α-**10**, 75684-29-6; β-**11**, 75684-30-9; α-**11**, 75684-31-0; β-**12**, 75684-32-1; α-**12**, 75684-33-2; **13**, 19124-37-9; **14** (C-6) derivative, 75626-76-5; **14** (C-3) derivative, 75626-77-6; **15** (C-6) derivative, 75626-78-7; **15** (C-3) derivative, 75626-79-8; **17**, 19124-38-0.

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Bromination of Tetraphenylethane and Triphenylethane

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Recently, the photochemical bromination of pentaphenylethane was shown to lead to triphenylmethyl bromide and diphenylmethyl dibromide.[1] These products were proposed to arise by the prior formation of the pentaphenylethyl radical and the corresponding ethyl bromide. The latter then dissociates to triphenylmethyl and bromodiphenylmethyl which account for the final products.

Strangely, there are no literature reports on the bromination of either tetraphenylethane or 1,1,2-triphenylethane. Since either of these could lead to a combination of six bromines and/or phenyls grouped about the central ethane, it seemed of some interest that these reactions be examined. The products could reflect on the operational balance between the steric factors, resonance stabilization, and bond strengths which appear to be of importance in

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