testing of this hypothesis requires establishing the stereochemistry of the silene precursors **2a,b**. Efforts aimed at the unambiguous determination of this stereochemistry are under way.

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Additivity in Split Cotton Effect Amplitudes of *p*-Phenylbenzyl Ethers and *p*-Phenylbenzoates

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We have been investigating micro methods to determine the site of oligosaccharide linkages[1,2] on the basis of the exciton chirality method.[3,4] During the studies we found that Cotton effect amplitudes or *A* values[5] of the split CD curves of hexopyranoside tri- and tetra-*p*-bromobenzoates respectively, *agreed with the sum of A values of the three and six dibenzoate units present.*[6] Namely, each benzoate chromophore on a pyranoside or any rigid system, e.g., trichothecenes,[7] adopts a specific predictable conformation, uniquely defining its position relative to others. However, the lability of benzoates to methanolysis, hydrolysis, transacylation, etc. prevents their direct application to oligosaccharide linkage analysis. An additivity relation has herein been demonstrated for the more stable phenylbenzyl *ether* chromophore, thus providing for a new class of exciton chirality chromophores applicable to glycosidic linkage studies.

Preliminary results with *p*-(methoxycarbonyl)benzylates, the chromophores of which are the same as those of benzoates, suggested that additivity may hold.[4] The *p*-phenylbenzyl chromophore best met the chromophoric criteria of strong UV ε, ease of formation, and stability; other chromophores which were abandoned after preliminary studies include *p*-cyanobenzyl and phenylpropynyl ethers. The PhBn ethers absorb at 253 nm and give split CD curves with extrema at 238 nm/260 nm (Figure 1). The Cotton effect *A* values of 15 tri- and tetra-PhBn hexopyranosides were calculated on the basis of additivity with very good agreement. These benzyl chromophores offer the further advantage of being oxidizable to corresponding *p*-phenylbenzoates, also exhibiting additivity, yet with a ca. 5-fold increase in *A* values.

Benzylations were carried out by stirring methyl glycosides, the OH groups of which were appropriately derivatized as methyl ethers, acetonides, etc., in DMF/THF (1:1) with NaH for 1 h, treating with PhBnBr in THF, and stirring 12 h, room temperature, 70% yield. UV measurements of several PhBn ethers led to the following ε values which were used as constants for determining the concentration of UV and CD solutions: mono 20 300, di 40 300, tri 61 000, tetra 82 300.

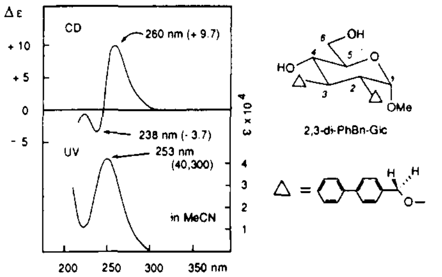
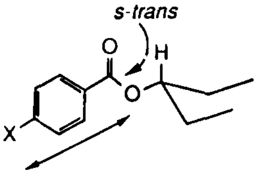


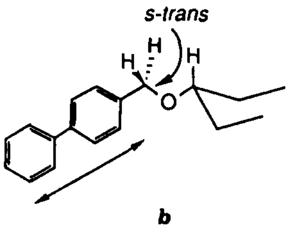
Figure 1. UV and CD of 2,3-di-*p*-phenylbenzyl ether of α-methyl glucoside, 15.4 μg/mL (29.3 pmol), in CH_3CN.

As in the case of *p*-bromobenzoates[6] all 18 di-PhBn ethers of α-methyl glucopyranoside, mannopyranoside, and galactopyranoside were prepared to provide the standard *A* values of bichromophoric units (Table I). The additivity relation was next tested by making all possible tri- and tetra-glucoside benzylates (Table II). Very good agreement is seen throughout between A_{obsd} and A_{calcd} in all 15 cases, despite the added possibility of conformational mobility, e.g., for **19**, A_{obsd} is −16.4, whereas A_{calcd} is +13.4 (for 2,3-, see **1**) − 25.4 (for 3,4-, **4**) − 5.0 (for 2,4-, **2**) = −17.0. Furthermore, the values are sufficiently different within each sugar class to be characteristic of the substitution pattern. This additivity relation suggests that, as in the case of benzoates (a), benzyl ethers favor an *s-trans* conformation around the C–O bond in Ph–CH_2–*O*–CH– (b) and that the 6-benzyl group with an additional C–C bond as well as other benzyl groups prefer specific conformations in each sugar.[8] In Table I, conformations of 6-PhBn groups are depicted to reflect the measured chirality signs of dibenzylate units involving this group. Conformation **b** is corroborated by molecular mechanics calculation (MM2) of (benzyloxy)cyclohexane which show that in its stablest conformation, **c**, the two benzyl methylene hydrogens flank the carbinyl hydrogen.



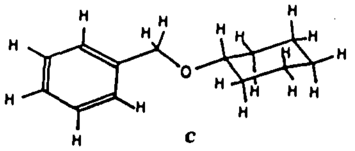
a

Benzoates



b

Phenylbenzyl ethers



c

The 1(e),2(e)- and 1(e),2(a)-di-*p*-bromobenzoates with dihedral angles of 60° have absolute *A* values of ca. 62,[6] but values for corresponding dibenzyl units vary from 3.9 (**7**, Table I) to 25.4 (**4**). One reason, although not the only one, is that the long PhBn chromophore extends further from the pyranose ring than the BrBz chromophore, resulting in a longer interchromophoric distance *R* in *ea* than in *ee* (it has been shown[3] that *A* is inversely proportional to the square of R). Although differences exist, the *benzylates and benzoates can thus be handled in a similar manner in exciton chirality problems.*

The longer R in PhBn ethers in comparison to BrBz leads to considerably smaller *A* values, a typical case being mannoside

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(5) *A* (amplitude) values denote the difference in Δε of split extrema; the sign is positive when the signs of first (longer wavelength) and second Cotton effects of the split CD curves are, respectively, positive and negative, and vice versa.

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Table I. *A* Values of Di-*p*-phenylbenzyl Ethers of Hexopyranosides, in CH$_3$CN

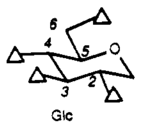
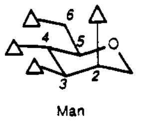
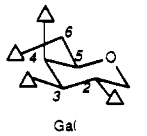
	 Glc		 Man		 Gal	
	entry	*A*	entry	*A*	entry	*A*
2,3-	**1**	+13.4 (1,2-ee)	**7**	−3.9 (1,2-ae)	**13**	+5.3 (1,2-ee)
2,4-	**2**	−5.0 (1,3-ae)	**8**	−3.6 (1,3-ae)	**14**	+6.9 (1,3-ea)
2,6-	**3**	−3.0	**9**	−3.5	**15**	0
3,4	**4**	−25.4 (1,2-ee)	**10**	−13.8 (1,2-ee)	**16**	+8.4 (1,2-ea)
3,6-	**5**	+3.9	**11**	+2.6	**17**	−2.6
4,6-	**6**	+16.1	**12**	+13.5	**18**	−13.7

Table II. Additivity in *A* Values of Tri- and Tetra-*p*-phenylbenzyl Ethers of Hexopyranosides, in CH$_3$CN

	glucoside			mannoside			galactoside		
	entry	obsd	calcd	entry	obsd	calcd	entry	obsd	calcd
2,3,4-	**19**	−16.4	−17.0	**24**	−21.6	−23.1	**29**	+19.4	+20.6
2,3,6-	**20**	+13.2	+14.3	**25**	−5.2	−4.8	**30**	+4.9	+2.7
2,4,6-	**21**	+9.7	+8.1	**26**	+7.2	+6.4	**31**	−8.1	−6.8
3,4,6-	**22**	−7.3	−5.4	**27**	+2.8	+2.3	**32**	−6.5	−7.9
2,3,4,6-	**23**	0	0	**28**	−9.8	−8.7	**33**	+5.1	+4.3

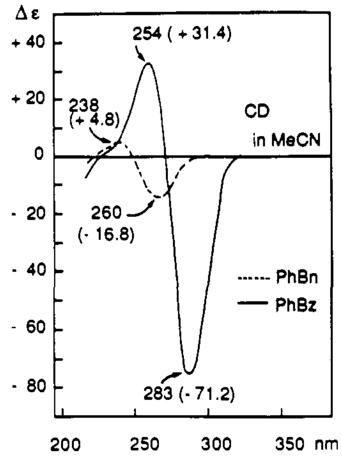


Figure 2. CD of 2,3,4-tri-*p*-phenylbenzyl ether (14.0 μg/mL or 20.2 pmol) and 2,3,4-tri-*p*-phenyl benzoate (9.0 μg/mL or 11.6 pmol) of α-methyl mannoside, in CH$_3$CN.

2,3,4-tribenzylate (Figure 2, *A* −21.6) vs. 2,3,4-tri-*p*-bromobenzoate (*A* −120[6]) or one-fifth sensitivity in the benzylate. However, oxidation of the ethers with ruthenium tetraoxide under conditions slightly modified from the original,[9] RuCl$_3$·3H$_2$O/NaIO$_4$ in CCl$_4$/CH$_3$CN, pH 7 aqueous buffer, 15–20 min, room temperature, converted sugar perbenzylates into corresponding benzoates in 60% yield,[10] with concomitant increase in *A* values *and* retention of additivity relation. The *A* values for following mannoside *p*-phenylbenzoates are (compare with corresponding benzylates in Table I), 2,3, −35.6, 2,4, −26.8; and 3,4, −60.5. The A_{calcd} for 2,3,4-triphenylbenzoate is −122.9, which compares well with A_{obsd} of −102.6 (Figure 2); note also 5-fold enhancement of *A* over tribenzylate.[11]

Simultaneous usage of two chromophores, the *p*-bromobenzoate (λ_{max} 244 nm) and *p*-methoxycinnamate (λ_{max} 311 nm), led to the finding that the additivity rule is valid not only for one-dimensional *A* values but more importantly for the entire *CD curve* of hexopyranoside acylates,[12] thus making *bichromophoric CD curves a characteristic of each sugar species*. In this paper we show that the *additivity rule can be extended to the more stable benzylates* and that if necessary a *ca. 5-fold enhancement in sensitivity* can be achieved by oxidation to corresponding benzoates. These findings form the basis of several micro methods under development for oligosaccharide structure studies.

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Preparation of the First η^2-Olefin Complex of a 4f-Transition Metal, (Me$_5$C$_5$)$_2$Yb(μ-C$_2$H$_4$)Pt(PPh$_3$)$_2$

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Insertion of an olefin into a metal–carbon bond is a fundamental and a reasonably well-known process in d- and f-transition metal organometallic chemistry.[1] It is generally assumed that coordination of the olefin to the metal center is a prerequisite to insertion, though no olefin complexes of an f-transition metal have been isolated, in contrast to the enormous number of olefin complexes of the d-transition metals as well as the monovalent coinage metals.[2] Recently the η^6-arene and η^2-acetylene complexes

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