Optical Rotatory Dispersion Studies on some Phenylazo-sugars

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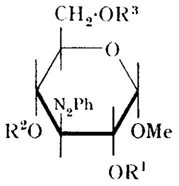
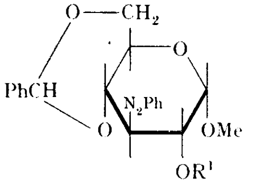
THERE has been little work on the optical rotatory dispersion (o.r.d.) of carbohydrates and their derivatives because of the lack of suitable chromophores in these molecules. We now report our work on the o.r.d. of the phenylazo-chromophore, part of a study on the chemistry of phenylazo-sugars.[1–3]



(I); $R^1 = R^2 = R^3 = H$
(II); $R^1 = Me$; $R^2 = R^3 = H$
(III); $R^1 = Ac$; $R^2 = R^3 = H$
(IV); $R^1 = Me$; $R^2 = R^3 = Ac$
(V); $R^1 = R^2 = R^3 = Ac$



(VI); $R^1 = H$
(VII); $R^1 = Ac$

Phenylazoalkanes have two absorption bands, a $\pi \rightarrow \pi^*$ transition at about 260 mμ ($\epsilon_{max.}$ 9000–12,000) and a $n \rightarrow \pi^*$ transition at about 400 mμ ($\epsilon_{max.}$ 100–200). Phenylazo-sugars have similar bands,[2] and we have found a Cotton effect curve in the 400 mμ region for all the compounds studied (I)–(VIII).[4]

For the monocyclic compounds the sign of the Cotton effect was positive for compounds (I)–(III), but negative for compounds (IV) and (V); compounds (VI) and (VII) gave positive curves. The curves were substantially the same in methanol and carbon tetrachloride, the amplitude of the Cotton effect being larger in the latter solvents.[5]

Infrared measurements suggest that the sign reversal of the Cotton effect between the two groups of monocyclic compounds is not due to conformational changes or to hydrogen-bonding effects. The most likely explanation is a significant reorientation of the N = N axis relative to the rest of the molecule.

Changes in both the absorption spectra and the o.r.d. curves of solutions of all compounds (I)–(VII) on prolonged exposure to light have been observed (cf. ref. 3).

These various effects are being further investigated by using other phenylazo-sugars and phenylazo-steroids.

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[1] R. D. Guthrie and L. Johnson, *J.*, 1961, 4166; G. J. F. Chittenden and R. D. Guthrie, *J.*, 1963, 3658; *Proc. Chem. Soc.*, 1964, 289.

[2] G. J. F. Chittenden and R. D. Guthrie, *J.*, 1964, 1045.

[3] G. J. F. Chittenden and R. D. Guthrie, *J.*, 1963, 2358.

[4] All compounds were prepared under normal laboratory conditions, without undue exposure to light.

[5] Solvent effects have been found in the circular dichroism spectra of compounds (VI) and (VII) (D. J. F. Hoy and E. M. Kosower, personal communication).