

The o.r.d. Curves of certain Benzenoid Chromophores

By AMNON YOGEV and YEHUDA MAZUR

(Department of Organic Chemistry, Weizmann Institute of Science, Rehovoth, Israel)

We have recorded the o.r.d. curves¹ of several ring-A-phenolic steroids and their derivatives in order to study the rotatory properties of the benzenoid chromophore. According to their substitution pattern, these compounds fall into three types, as illustrated by Figure 1. While the phenol (I) shows a plain Cotton-effect curve (observed also in the phenol IV), the phenol (II) exhibits a strongly positive Cotton effect at the lower-wavelength region and a weaker one in the higher-wavelength region; whereas the o.r.d. curve of the phenol (III) consists of two distinct Cotton effects superimposed on one other.

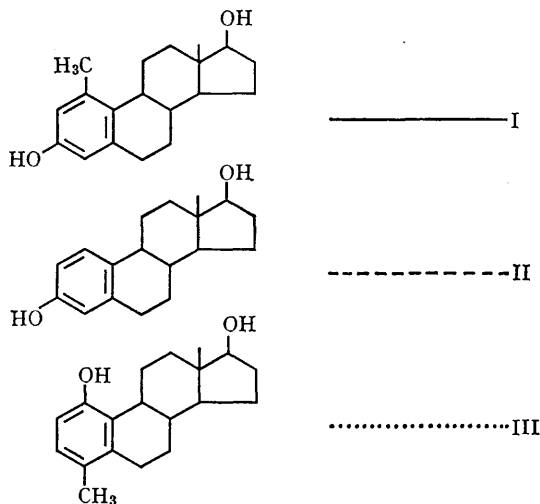
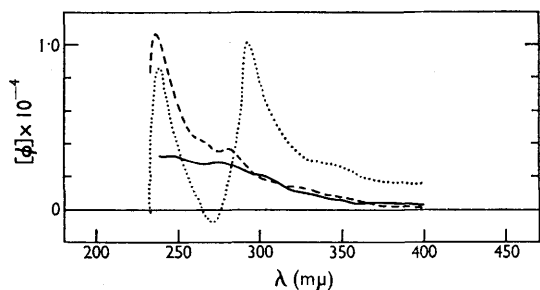
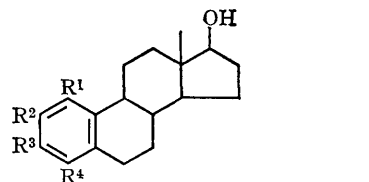


FIGURE 1

The corresponding methyl ethers and sodium phenolates show o.r.d. curves similar to the parent phenols, the peaks of the phenolates being shifted bathochromically by *ca.* 30 $m\mu$.

Non-oxygenated benzene derivatives possess optically active transitions of low intensity, attributed to a combination of an electric dipole moment vector in the plane of the ring and a magnetic moment perpendicular to this plane.² Accordingly compounds (V) and (VI) show a weak Cotton effect at *ca.* 260 $m\mu$ ($[\Phi] = ca\ 600^\circ$, superimposed on a positive plain curve with $[\Phi]$ of the same order of magnitude). In contrast, the high Cotton effects observed in the oxygenated benzene chromophore^{2,3} should be due to the $n \rightarrow \pi^*$ transition of the oxygen's lone-pair electrons, with a magnetic transition moment directed roughly along the C-O axis. Only the component of the electric transition moment along the axis of the magnetic moment is responsible for the rotatory power. This component is determined by both the magnitude and the direction of the electric transition vector, and therefore is very sensitive to the substitution pattern. The substitution pattern thus affects the o.r.d. curves (and particularly the Cotton effects) even more than it affects the absorption intensity of the 260–300 $m\mu$ transitions of the benzenoid chromophore.⁴



		R ₁	R ₂	R ₃	R ₄
(I)	..	CH ₃	H	OH	H
(II)	..	H	H	OH	H
(III)	..	OH	H	H	CH ₃
(IV)	..	H	OH	H	CH ₃
(V)	..	H	H	H	H
(VI)	..	H	H	H	CH ₃

(Received, July 16th, 1965; Com. 445.)

¹ The o.r.d. measurements were performed on a JASCO Model ORD/UV-5 instrument of the Japan Spectroscopic Co. Ltd., in ethanol or in dioxan solutions, using cells of 0.1 cm. width.

² A. Moscowitz, A. Rosenberg, and A. E. Hansen, *J. Amer. Chem. Soc.*, 1965, **87**, 1813; L. Verbit, *ibid.*, 1965, **87**, 1617.

³ T. M. Hooker and C. Tanford, *J. Amer. Chem. Soc.*, 1964, **86**, 4989.

⁴ L. Doub and J. M. Vandebelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714; L. Doub and J. M. Vandebelt, *ibid.*, 1949, **71**, 2414; H. H. Jaffe and M. Orchin, "Theory and Application of the Ultra-violet spectroscopy," J. Wiley and Sons, Inc., New York, N.Y., 1962, pp. 242–270.