

### 650. The Relation between the Rotatory Power of Asymmetric Ketones and Intensity-borrowing by the Carbonyl Absorption at 3000 Å.

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The rotatory powers of asymmetric ketones are found to approximate to a theoretical relationship requiring the dependence of the rotational strength upon the square root of the dipole strength of the intensity enhancement of the carbonyl absorption at 3000 Å.

WOODWARD and KOVACH in 1950 suggested<sup>1</sup> that the high rotation and abnormally large carbonyl absorption of santonide have a common basis. During the past decade the conditions under which the carbonyl absorption becomes enhanced have been extensively investigated by Cookson and his co-workers,<sup>2</sup> who have shown further that

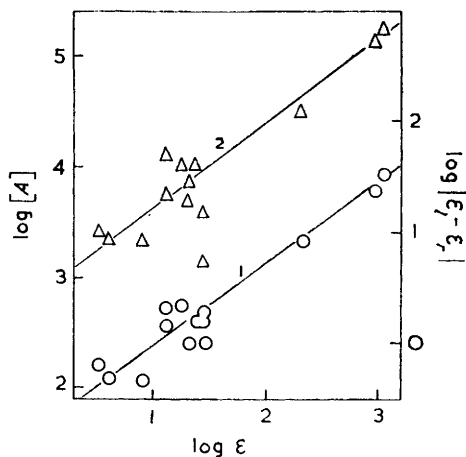


FIG. 1. The relation between the intensity enhancement ( $\epsilon$ ) of the carbonyl absorption at 3000 Å and (a) the circular-dichroism extinction coefficient difference ( $|\epsilon_1 - \epsilon_r|$ ) (curve 1) and (b) the amplitude of the Cotton effect ( $[A]$ ) (curve 2), in the series of optically active carbonyl compounds.

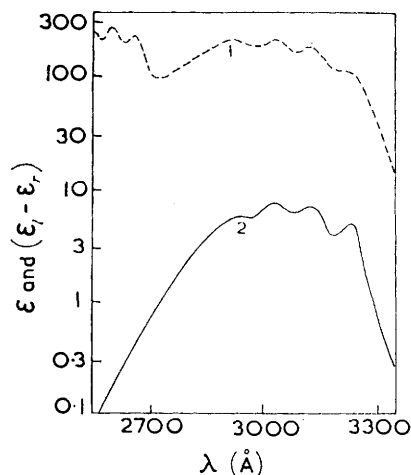


FIG. 2. The ultraviolet absorption spectrum (Curve 1) and the circular dichroism (Curve 2) of 3 $\alpha$ -phenylcholestan-2-one.

the rotatory power of asymmetric ketones increases as the intensity of the carbonyl  $n \rightarrow \pi^*$  band at 3000 Å becomes greater.<sup>2,3</sup>

The most reliable experimental measure of the rotatory power of an absorption band in the electronic spectrum of an optically active compound is provided by the band area of the circular dichroism absorption, the amplitudes of anomalies in the optical rotatory dispersion curves, which are more frequently used,<sup>4</sup> having their values modified by background rotation. A spectrophotometer designed to measure circular dichroism, the differential absorption of left- and right-handed circularly polarized light by the chromophores of optically active compounds, has been constructed and used to study the rotatory power of the carbonyl chromophore.

Classical measurements of the circular dichroism of aldehydes and ketones cover two

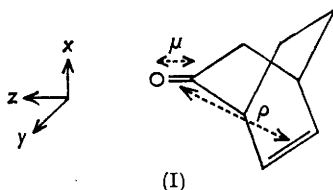
<sup>1</sup> Woodward and Kovach, *J. Amer. Chem. Soc.*, 1950, **72**, 1009.

<sup>2</sup> Cookson, *J.*, 1954, 282; Cookson and Dandegaonker, *J.*, 1955, 352; Cookson and Wariyar, *J.*, 1956, 2302; Birnbaum, Cookson, and Lewin, *J.*, 1961, 1224.

<sup>3</sup> Cookson and Hudec, *J.*, 1962, 429.

<sup>4</sup> Djerassi, "Optical Rotatory Dispersion," McGraw Hill, New York, 1960.

main groups of compounds, the santonides,<sup>5</sup> and terpene<sup>6-11</sup> and sugar<sup>12</sup> derivatives. The 3000 Å band intensities and the rotatory powers are large in the first group and small in the second (Table). In order to link the data for the two groups, the circular dichroism of 3 $\alpha$ -phenylcholestan-2-one, which has a carbonyl absorption of moderate intensity,<sup>3</sup> has been measured (Table). The absorption ( $\epsilon_{\max}$ , 11) of cyclohexanone<sup>13</sup> being aken as at reference for the estimation of the borrowing of intensity in asymmetric ketones, the data (Table) indicate that the rotatory power of the carbonyl chromophore is proportional to the intensity enhancement of the 3000 Å band raised to the power of 0.7 (Fig. 1). Similar relations are observed whether the circular dichroism (curve 1) or the amplitude of the Cotton effect (curve 2) is used as a measure of rotatory power, though there is more scatter of points in the latter relation owing to the uncertain effect of background rotation.



It has been shown<sup>14</sup> that in the ketone (I) the intensity of the absorption at 3000 Å is enhanced owing to the mixing of the electric dipole forbidden  $n \rightarrow \pi^*$  transition of the

TABLE.

The wavelengths ( $\lambda_{\max}$ ), maximum extinction coefficients ( $\epsilon_{\max}$ ), and maximum circular-dichroism extinction coefficient differences ( $|\epsilon_1 - \epsilon_r|$ ), of the carbonyl absorption in the spectra of optically active ketones, and the molecular rotation amplitude,  $[A]$ , of the anomaly in the optical rotatory dispersion curve in circular degrees.

No.	$\lambda_{\max}$ . (Å)	$\epsilon_{\max}$ .	$ \epsilon_1 - \epsilon_r $	$[A]$	Ref.	
1	3-Methylcyclohexanone	2905	14.25	0.642	2570	7
2	Campholic aldehyde	2950	15	0.70	2170	8
3	Carvomenthone	2886	19	0.47	2038	9
4	Camphor	2950	24	1.5	5800	6
5	Camphor- $\beta$ -sulphonic acid	2840	35	1.535	10,300	10
6	Camphorquinone	4780	39	1.95	1290	11
7	Pulegone	3240	40	1.53	>5260	7
8	D-Glucose penta-acetate	2920	32	1.0	4880	12
9	D-Galactose penta-acetate	2900	29	2.25	9750	12
10	D-Fructose penta-acetate	2830	39	1.0	3900	12
11	L-Arabinose tetra-acetate	2900	32	1.0	7000	12
12	L-Fucose tetra-acetate	2935	24	2.15	13,200	12
13	3 $\alpha$ -Phenylcholestan-2-one	2990	220	8.8*	30,300	3
14	Santonide	3000	1000	24	139,000	5
15	Parasantonide	3000	1170	35	165,000	5

\* Present work.

carbonyl group with an allowed charge-transfer transition of a  $\pi$ -electron from the carbon-carbon double bond to the antibonding  $\pi$ -orbital of the carbonyl group. A similar mechanism is probably responsible for the smaller intensity enhancement<sup>2</sup> of the carbonyl

<sup>5</sup> Mitchell and Schwarzwald, *J.*, 1939, 889.

<sup>6</sup> Kuhn and Gore, *Z. phys. Chem.*, 1931, B, 12, 389.

<sup>7</sup> Lowry, Simpson, and Allsop, *Proc. Roy. Soc.*, 1937, A, 163, 483.

<sup>8</sup> Lowry and Baldwin, *J.*, 1937, 233.

<sup>9</sup> Lowry and Lishmund, *J.*, 1935, 709.

<sup>10</sup> Lowry and French, *J.*, 1932, 2645.

<sup>11</sup> Lowry and Gore, *Proc. Roy. Soc.*, 1932, A, 135, 15; Lowry and Simpson, *J.*, 1936, 1156.

<sup>12</sup> Baldwin, Wolfram, and Lowry, *J.*, 1935, 696.

<sup>13</sup> Benson and Kistiakowsky, *J. Amer. Chem. Soc.*, 1942, 64, 80.

<sup>14</sup> Labhart and Wagniere, *Helv. Chim. Acta*, 1959, 42, 2219.

absorption in ketones substituted with alkyl groups or with atoms bearing lone-pair electrons, since paraffins have ionization potentials only 0.9–1.1 eV higher than those of the corresponding olefins, and alkyl halides, ethers, and amines have intermediate or lower ionization potentials.<sup>15</sup> The condition for the mixing of the carbonyl  $n \rightarrow \pi^*$  and the charge-transfer transition is that the orbital from which the charge-transfer transition originates shall overlap both the  $2p_y$  lone-pair orbital of the oxygen atom and the  $\pi_x$  orbitals of the carbonyl group.<sup>2,3,14</sup> This condition confers rotatory power upon the mixed transition, provided that there is only one donor group or that two such groups are placed asymmetrically with respect to the nodal planes of the oxygen lone-pair orbital and the carbonyl antibonding  $\pi$ -orbital.

The absorption at 3000 Å of asymmetric ketones is due to the transition of an electron to the carbonyl antibonding  $\pi$ -orbital from a mixed orbital,  $\psi$ . It can be written,

$$\psi = a2p_y(O) + b\phi, \quad (1)$$

where  $2p_y(O)$  and  $\phi$  refer, respectively, to the oxygen lone-pair orbital and the donor orbital from which the charge-transfer originates, and  $a$  and  $b$  are coefficients such that  $a \gg b$  and  $(a^2 + b^2) = 1$ . The value of  $a$  is always near to unity in the series considered. The rotational strength,  $R$ , of the transition is given by the scalar product of the magnetic and the electric dipole transition moments.<sup>16</sup> The  $n \rightarrow \pi^*$  component of the mixed transition has a magnetic dipole transition moment,  $\mu$ , directed along the carbonyl axis, and the charge-transfer component has an electric dipole transition moment,  $\rho$ , directed at an angle  $\theta$  to the carbonyl bond axis (e.g., I), giving

$$R = ab\mu\rho \cos \theta. \quad (2)$$

The intensity enhancement of the ketone absorption at 3000 Å depends upon the dipole strength,  $D$ , of the charge-transfer component of the mixed transition, where

$$D = (b\rho)^2, \quad (3)$$

so that

$$R = a\mu \cos \theta \cdot \nu D. \quad (4)$$

Thus the rotatory power of asymmetric ketones should be proportional to the square root of the intensity enhancement of the absorption at 3000 Å if  $\theta$  does not vary greatly from compound to compound. Models indicate that in the ketones with a single or a dominant asymmetric donor substituent,  $\theta \sim 40^\circ$ , and these compounds (Nos. 1, 13, 14, and 15, Table) span the whole range of rotatory powers and intensity enhancements considered.

The experimental exponent (0.7) relating rotatory power to intensity-borrowing is larger than the theoretical (0.5) partly because extinction coefficients rather than band areas have been plotted in Fig. 1. Band half-widths, where available, average 5300  $\text{cm}^{-1}$  for the absorption bands and 4300  $\text{cm}^{-1}$  for the circular-dichroism bands, suggesting a value of 0.6 for the experimental exponent based upon band areas.

#### EXPERIMENTAL

The circular dichroism spectrophotometer was constructed from a Hilger Uvispek silica-prism monochromator fitted with tungsten and hydrogen-arc light sources. Monochromatic light from the exit slit passes successively through a quartz lens, a Rochon prism, a Fresnel rhomb of glass or fused silica, and the sample cell, the light coming to a focus at a slit immediately in front of the IP 28 photomultiplier detector. The Rochon prism is mounted between two ball-races, and can be rotated about its longitudinal axis between two stops, so that the plane of the linearly polarized light is at an angle of  $\pm 45^\circ$  to the face edges of the Fresnel rhomb from which the light emerges either left- or right-circularly polarized. After amplification, the signal from the detector is fed to a millivolt pen recorder, giving either

<sup>15</sup> Watanabe, *J. Chem. Phys.*, 1957, **26**, 542.

<sup>16</sup> Condon, Altar, and Eyring, *J. Chem. Phys.*, 1937, **5**, 753; Moffitt and Moscovitz, *J. Chem. Phys.*, 1959, **30**, 648.

the absolute percentage transmission or the differential percentage transmission of the two circular components. The circular dichroism of 3 $\alpha$ -phenylcholestan-2-one was measured in ethanol solution.

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