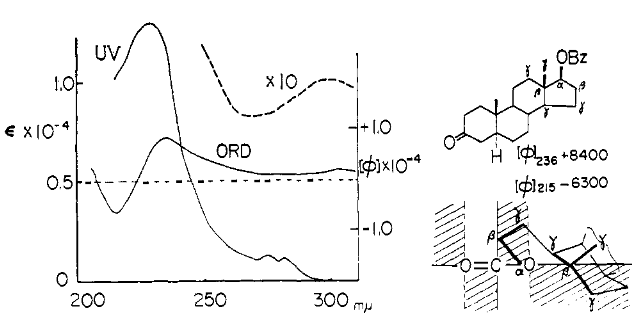

Figure 3. The benzoate Cotton effect of 3-oxoandrostane 17β-benzoate (EtOH). The Cotton effect of the ketone group is evident in the curve on the 10-fold expanded scale.

The presence of saturated ketone groups does not interfere with the interpretation, since Cotton effects due to ketone and benzoate groups differ greatly in position and intensity (Figure 3): the amplitude of the 290-mμ ketone Cotton effect is usually 5–50, whereas that of the 225-mμ benzoate group is 100–300. Correct predictions can be made in some cases even when the strongly optically active enone group is present, *e.g.*, the difference curve between the ORD curves of taxinine A[10,11] and its benzoate (Figure 1) (both with $a = ca.$ 2000 around 250 mμ) clearly shows the expected positive Cotton effect centered at 225 mμ, $a = +165$. Where results are ambiguous because of overlap of the substrate and benzoate absorptions, the benzoate absorption can be shifted to longer wavelengths by appropriate *para* substituents[7] (*e.g.*, entry 15).

Although the scope of application of the present benzoate sector rule still remains to be clarified, a limiting case is when the asymmetric perturbation of the benzoate chromophore is insufficient to give rise to a Cotton effect, such as in cholestan-3β-ol and isoborneol (*endo*-OH); otherwise it appears to be widely applicable.[12]

**Acknowledgments.** We are grateful to Drs. P. Crabbé, Shô Itô, K. Takeda, and T. Wada for generous gifts of the samples listed in Table I.

[10] The absolute configuration of taxinine has been established by chemical correlations and X-ray analysis: M. Dukes, D. H. Eyre, J. W. Harrison, and B. Lythgoe, *Tetrahedron Letters*, 4765 (1965), and M. Shiro, T. Sato, H. Koyama, Y. Maki, K. Nakanishi, and S. Uyeo, *Chem. Commun.*, 98 (1966), respectively.

[11] H. C. Chiang, M. C. Woods, Y. Nakadaira, and K. Nakanishi, *ibid.*, 1201 (1967).

[12] This work has been supported in part by the National Institutes of Health, Public Health Service Research Grant No. CA 08394.

[13] Tanabe Pharmaceutical Co., Saitama, Japan.

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## Optical Rotatory Power of the Benzoate Group

*Sir:*

The benzoate sector rule, a method for determining the absolute configuration of cyclic secondary alcohols, has been described in the preceding communication.[1] The theoretical aspects of the sector rule is discussed in the following.

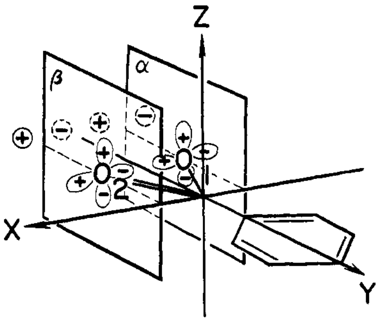

Figure 1. Signs of the upper sectors.

As the benzoate chromophore is inherently symmetric, the observed Cotton effect necessarily arises from the asymmetric perturbation of a substituent. The benzoate chromophore exhibits three $\pi \rightarrow \pi^*$ absorption bands in the ultraviolet region, *i.e.*, at 280 mμ (ε 1000) due to the $^1A_{1g} \rightarrow {}^1B_{2u}(^1L_b)$ transition[2] of the benzene ring, at 230 mμ (ε 14,000) due to an intramolecular charge-transfer transition,[3–5] and at 195 mμ (ε 40,000) due to the $^1A_{1g} \rightarrow {}^1B_{1u}(^1L_a)$ transition.[6] In these transitions, the first and second absorption bands have the transition moments along the short and long axis of the benzoate chromophore,[7] respectively. The benzoates of optically active alcohols[8] exhibit a Cotton effect only at *ca.* 225 mμ; no Cotton effect was observed at the other absorption bands.

The fact that the observed Cotton effect is indeed due to the $\pi \rightarrow \pi^*$ intramolecular charge-transfer transition and not due to an $n \rightarrow \pi^*$ transition hidden in the strong absorption band was ascertained by observing the red shift caused by *para* substituents. As indicated in Table I, the shifts in the Cotton effect parallel those of the ultraviolet absorption maxima, and this provides strong support for the transition being $\pi \rightarrow \pi^*$. If the bands under consideration originated from an $n \rightarrow \pi^*$ transition a blue shift would have been expected.[9]

**Table I.** Cotton Effects of *para*-Substituted Benzoates of Cholesterol[a]

| Substituent | Uv $\lambda_{max}$, mμ | ORD, deg 1st extremum | ORD, deg 2nd extremum | *a* |
|---|---|---|---|---|
| $N(CH_3)_2$ | 311.2 | $[\phi]_{316}$ +6100 | $[\phi]_{270}$ −5400 | +115 |
| $NH_2$ | 293.8 | $[\phi]_{300}$ +8100 | $[\phi]_{262}$ −9500 | +176 |
| $OCH_3$ | 256.1 | $[\phi]_{262}$ +9000 | $[\phi]_{230}$ −9500 | +185 |
| Cl | 240.2 | $[\phi]_{246}$ +11,300 | $[\phi]_{220}$ −9400 | +207 |
| H | 229.2 | $[\phi]_{235}$ +8400 | $[\phi]_{215}$ −3600 | +120 |
| CN | 239.5 | $[\phi]_{245}$ +4600 | $[\phi]_{216}$ −10,000 | +146 |

[a] Solvent: methanol–dioxane (9:1).

[1] N. Harada, Mo. Ohashi, and K. Nakanishi, *J. Am. Chem. Soc.*, **90**, 7349 (1968).

[2] P. Crabbé and W. Klyne, *Tetrahedron*, **23**, 3449 (1967).

[3] S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); S. Nagakura, *ibid.*, **23**, 1441 (1955); J. Tanaka and S. Nagakura, *ibid.*, **24**, 1274 (1956).

[4] J. Tanaka, S. Nagakura, and M. Kobayashi, *ibid.*, **24**, 311 (1956).

[5] Alternatively, this band has been assigned to the $^1A_{1g} \rightarrow {}^1B_{1u}$ transition of the benzene chromophore: H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962.

[6] L. Verbit and Y. Inouye, *J. Am. Chem. Soc.*, **89**, 5717 (1967).

[7] J. Tanaka, *Bull. Chem. Soc. Japan*, **36**, 833 (1963).

[8] The benzoate sector rule so far only applies to cyclic secondary alcohols. However, primary alcohol benzoates also exhibit the 225-mμ Cotton effect, provided the optical center is not too far removed from the hydroxyl group; extension of the present rule is being carried out.

[9] The $n \rightarrow \pi^*$ band has not been observed for benzoic acid but has been measured in various solvents for the *para*-substituted acetophenones.[4]

The data in Table I are of practical value since they allow a choice in the wavelengths of the Cotton effects and thus greatly facilitate measurements when the alcohol itself has an optically active absorption, *e.g.*, benzenoid, enone, overlapping that of the benzoate chromophore.[10]

The optical rotatory power or rotational strength $R_{\pi\pi^*}$ is proportional to the imaginary part of the scaler product of the electric transition moment and magnetic transition moment[11] (eq 1). Since the intramolecular charge-transfer transition

$$R_{\pi\pi^*} = Im[(\psi_\pi|\mathbf{P}|\psi_{\pi^*})(\psi_{\pi^*}|\mathbf{M}|\psi_\pi)] \tag{1}$$

$$\psi_\pi{}^0\ (=\sum_r C_{\pi r}(\chi_{2p_z})_r) \rightarrow \psi_{\pi^*}{}^0\ (=\sum_r C_{\pi^* r}(\chi_{2p_z})_r)$$

has its electric transition moment along the $y$ axis,[12] the magnetic transition moment directed along the $y$ axis makes a contribution to the optical rotation. If the atomic orbital of the $\pi$-molecular orbital is approximated by the Slater type orbital, the magnetic moment operation for the atomic orbital can be evaluated, for example, as in eq 2.[13,14] The rotational strength

$$\mathbf{M}\chi_{2p_z} = \frac{e\hbar}{2mci}[\mathbf{i}\chi_{2p_y} - \mathbf{j}\chi_{2p_x}] \tag{2}$$

calculated by first-order perturbation then becomes

$$R_{\pi\pi^*} = Im\left[\frac{-\mathbf{j}e\hbar}{2mci}(\psi_\pi{}^0|\mathbf{P}|\psi_{\pi^*}{}^0)\left\{\sum_{j\neq\pi^*}\frac{\int\psi_j{}^0V\psi_{\pi^*}{}^0\mathrm{d}\tau}{E_{\pi^*}{}^0 - E_j{}^0}\times\right.\right.$$
$$\int\psi_j{}^0\sum_r C_{\pi r}(\chi_{2p_x})_r\mathrm{d}\tau - \sum_{i\neq\pi}\frac{\int\psi_i{}^0V\psi_\pi{}^0\mathrm{d}\tau}{E_\pi{}^0 - E_i{}^0}\times$$
$$\left.\left.\int\psi_i{}^0\sum_r C_{\pi^* r}(\chi_{2p_x})_r\mathrm{d}\tau\right\}\right]$$

where $\psi_i{}^0$ and $\psi_j{}^0$ are either the orbitals introduced by the electrostatic perturbation $V$ mainly due to the incomplete screening of nuclei of asymmetric substituents and are limited to those having nonzero overlap integrals with $\chi_{2p_z}$ (electrostatic perturbation) or the orbitals of asymmetric substituent itself which overlap with $\psi_{\pi^*}{}^0$ and $\psi_\pi{}^0$ orbitals (overlap perturbation).[11,15]

If it is assumed that the two oxygen atoms have similar electronic properties and are effectively perturbed because of the proximity of the asymmetric center, the rotational strength $R_{\pi\pi^*}$ will be governed by the oxygen orbitals, $\chi_{2p_z}$ and $\chi_{2p_x}$. The first term of the magnetic transition moment then becomes

$$\sum_{j\neq\pi^*}\underbrace{\frac{\int\psi_j{}^0V\{C_{\pi^*O_1}(\chi_{2p_z})_{O_1} + C_{\pi^*O_2}(\chi_{2p_z})_{O_2}\}\mathrm{d}\tau}{E_{\pi^*}{}^0 - E_j{}^0}}_{A}\times$$
$$\underbrace{\int\psi_j{}^0\{C_{\pi O_1}(\chi_{2p_x})_{O_1} + C_{\pi O_2}(\chi_{2p_x})_{O_2}\}\mathrm{d}\tau}_{B}$$

where $C_{\pi^*O_1} \approx C_{\pi^*O_2}$ and $C_{\pi O_1} \approx C_{\pi O_2}$. In the case of electrostatic perturbation, the sign of the term $A$ depends on the position of the asymmetric substituent in the eight spaces divided by the nodal planes of the orbitals $\chi_{2p_z}$ and $\psi_j{}^0$ (Figure 1). On the other hand, the term $B$ is fixed in sign without regard to the position of substituent. In the case of overlap perturbation, $A$ will be of opposite sign in the two spaces divided by plane $xy$, and $B$ also alters its sign in the four sectors divided by planes $\alpha$, $\beta$, and $yz$. The same situation also holds for the second term. Therefore, the product of $A$ and $B$, *viz.*, the rotational strength $R_{\pi\pi^*}$, alternates its sign, in rough approximation, from sector to sector as illustrated in Figure 1. Since the present qualitative discussion is based on a simple LCAO-MO treatment, and the orbital $\psi_j{}^0$ may dominantly be the lone-pair orbitals in the case of electrostatic perturbation, an unambiguous prediction of the absolute sign and a quantitative definition of the sector boundaries require more exact wave functions and knowledge pertaining to the asymmetric perturbation[16] and structures of lone-pair orbitals.

The fact that no Cotton effect is detected in the $\pi \rightarrow \pi^*$ transition at 280 m$\mu$ can be accounted for by the properties of the transition, namely, the wave function related to the $^1L_b$ transition is localized in the benzene ring, and therefore, owing to the large distance from the asymmetric center responsible for the perturbation, the rotational strength is almost zero. The same consideration applies to the $^1L_a$ transition. In contrast, due to the strong contribution of the COO group, the wave function related to the 230-m$\mu$ transition is effectively perturbed by the substituent and a Cotton effect is observed.[17]

**Acknowledgments.** We are indebted to Dr. Y. Amako of our department for helpful discussions.

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[10] See entry 15 in Table I, ref 1.

[11] W. J. Kauzmann, J. E. Walter, and H. Eyring, *Chem. Rev.*, **26**, 339 (1940); A. Moscowitz, *Advan. Chem. Phys.*, **4**, 67 (1962).

[12] The direction of the transition moment of this band in benzoic acid is actually tilted by 6.5° from the $y$ axis toward the carbonyl group.[7]

[13] J. C. Tai and N. L. Allinger, *J. Am. Chem. Soc.*, **88**, 2179 (1966).

[14] Y.-H. Pao and D. P. Santry, *ibid.*, **88**, 4157 (1966).

[15] G. Wagnière, *ibid.*, **88**, 3937 (1966).

[16] The various asymmetric perturbations have been discussed for the inherently symmetric system in ref 11 and 15.

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## Perchlorotropone

*Sir:*

We have synthesized hexachlorotropone (II), the first perhalogenated tropone, by direct photoisomerization of hexachlorobicyclo[3.2.0]hepta-3,6-dien-2-one (I).[1] Although the photoisomerization of substituted tropones to bicycloheptadienones[2] and the further phototransformations of the products have been extensively studied,[3] to our knowledge the present case is the first example of the reverse reaction.

Irradiation of a dilute (1–2%) dichloromethane solution of I in a quartz vessel, using low-pressure mercury vapor lamps in a Griffin–Srinivasan reactor,[4]

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[1] A. Roedig and L. Hornig, *Ann.*, **598**, 208 (1956).

[2] (a) K. F. Koch, *Advan. Alicyclic Chem.*, **1**, 258 (1966); (b) D. J. Pasto in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 155 ff.

[3] O. L. Chapman and J. D. Lassila, *J. Am. Chem. Soc.*, **90**, 2449 (1968), and references therein.