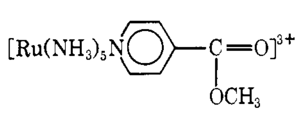
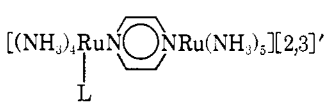
an energy approximately[5] four times that. The factor 4 can arise from the quadratic dependence of the energy on the extent of distortion of the ion's first coordination sphere.[6] Marcus has estimated[7] this distortion to contribute approximately 8 kcal to $\Delta F^{\ddagger}$ for self-exchange in the $Fe(H_2O)_6^{2+}$–$Fe(H_2O)_6^{3+}$ and $Co(H_2O)_6^{2+}$–$Co(H_2O)_6^{3+}$ systems. An energy cost somewhat less than this would be expected for the present system involving as it does only changes in the t_{2g} energy levels. If the energy barrier measured by the infrared transition is interpreted as being four times $\Delta F^{\ddagger}$ for internal electron transfer, a self-exchange rate of 3×10^9 sec^{-1} is calculated for [2,3]. This seems reasonable in comparison to a second-order rate constant of 10^6 M^{-1} sec^{-1} measured[8] for electron transfer between **1** and **6** (this value has been corrected for the effect[9] of $\Delta F°$). When allowance is made for the energy required to bring the reactants together, the second-order rate constant referred to would convert to a considerably greater first-order constant for electron transfer within the collision complex.



6

Observations made with unsymmetrical species of type **7** in D_2O solutions strongly support our interpretation of the long wavelength band. First we prepared **8** by adding *cis*-$(NH_3)_4Ru(OD_2)_2^{2+}$ to a solution of **1**. When the association reaction was complete as judged by the absorption spectrum in the visible region, $S_2O_8^{2-}$ was added as oxidant to prepare [2,3]′, L = D_2O. The long wavelength band is shifted only slightly in this complex, the maximum appearing at 1530 mμ. The shift is much more pronounced, however, in complexes prepared by substituting other ligands for D_2O. A complex where L = pyrazine was prepared by making a solution of [2,2]′, L = D_2O, 1 M in pyrazine, allowing the reaction to go to completion to give [2,2]′, L = pyrazine, and then adding $S_2O_8^{2-}$ as oxidant to give [2,3]′, L = pyrazine. In this solution, the new band appeared at 1160 mμ. A *cis*-chloro dimer was prepared by oxidizing [2,2]′, L = D_2O, in 2 M sodium chloride. Presumably the first product of the oxidation is the [2,3] aquo dimer which then equilibrates with the medium. This transformation can actually be observed in the near-infrared spectra. At first, two maxima are evident. One, at 1530 mμ, attributed to the *cis*-aquo dimer, disappears over 0.5 hr to give a single maximum centered at 1450 mμ, attributable to



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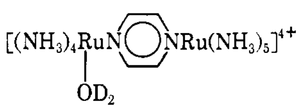

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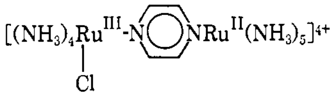

9

It is notable that the shift observed for the near-infrared band when ammonia is replaced by chloride (0.1 V) or by pyrazine (0.3 V) parallels the difficulty of electron transfer as measured in equilibrium processes. This trend is expected on the basis of our interpretation of the long wavelength band. In [2,3]′, L = Cl^-, it is more difficult to reduce Ru(III) bound to chloride than to ammonia. In [2,3]′, L = pyrazine, the presence of a back-bonding ligand makes the oxidation of Ru(II) more difficult than for the pentaammine.

The interpretation advanced for the long wavelength band in the [2,3] species depends on the supposition that the two Ru atoms in the species are not equivalent though, as already acknowledged, electron transfer is expected to be rapid. To the extent that the interpretation is successful in explaining the observations, it supports the basic assumption. The assumption finds added support in the observation that the $t_{2g} \rightarrow \pi^*$ transition in [2,3] differs in energy only slightly from that in [2,2]. Apparently much stronger coupling is needed than is provided by the π-orbital system of the pyrazine bridging group to bring the Ru atoms into equivalent configurations. As measured by the rates for spontaneous electron transfer, the energies required to bring Ru(II) and Ru(III) into equivalent configurations decreases as NH_3 is replaced by back-bonding ligands,[8,10,11] and with more back-bonding ligands in the coordination sphere, the two atoms in the +5 ion may be equivalent. Work is in progress in an effort to prepare an ion analogous to [2,3] from the nucleus $Ru(bipy)_2(H_2O)_2$.

Warning. Perchlorate salts of ruthenium ammines are hazardous and should be handled only in milligram quantities unless elaborate precautions appropriate to manipulating sensitive and explosive materials are taken.

Acknowledgment. Financial support for this research by the National Institutes of Health, Grant No. GM 13638-02-03, by NIH Predoctoral Fellowships for C. Creutz, 1967 to date, and to the National Science Foundation for purchase of the Cary-14 spectrometer is gratefully acknowledged.

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[5] "Approximately" for the reason, among others, that the distortion called for in the spontaneous electron transfer may differ in symmetry from that which results from radiation-induced electron transfer.

[6] (a) P. George and J. S. Griffith, "The Enzymes," Vol. 1, P. D. Boyer, *et al.*, Ed., Academic Press, New York, N. Y., 1959, p 347; (b) R. A. Marcus, *Discussions Faraday Soc.*, **29**, 21 (1960); (c) N. S. Hush, *Progr. Inorg. Chem.*, **8**, 391 (1967).

[7] R. A. Marcus, *Trans. N. Y. Acad. Sci.*, **19**, 423 (1957).

[8] R. G. Gaunder, unpublished observations.

[9] R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

[10] T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968).

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A Method for Determining the Chiralities of Optically Active Glycols

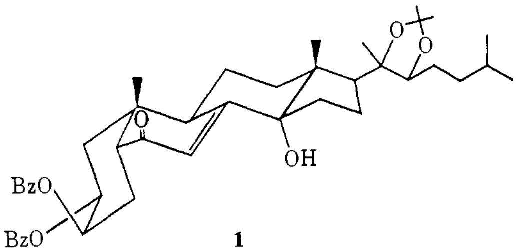
Sir:

The chirality of glycols can be determined from the sign of the strong $\pi \rightarrow \pi^*$ Cotton effect of its dibenzoate

Table I. CD of Dibenzoates

Entry	Compound[a,b]	Chirality	Δε (mμ)[c] 1st	Δε (mμ)[c] 2nd	Solvent[d]
1	5α-Cholestane 2α,3β- (W)	(−)	−13.9 (234)	+14.6 (219)	E–D
2	5α-Cholestane 2β,3β-	(+)	+11.5 (232)	−2.5 (212)	E–D
3	5α-Cholestane 2β,3α- (W)[e]	(+)	+11.0 (230)	[210][f]	E
4a	Cholest-5-ene 3β,4β-	(−)	−10.2 (232)	+11.4 (218)	M–D
4b	Cholest-5-ene 3β,4β-di-*p*-chlorobenzoyloxy-	(−)	−18.9 (247)	+21.0 (229)	M–D
5	5α-Cholestane 3β,6β-di-*p*-chlorobenzoyloxy-	(−)	−16.4 (246)	+12.1 (231)	E–D
6	Ponasterone A 20,22-		[+1.8 (327)	−3.9 (248)][h]	
	acetonide 2,3-[g]	(−)	−14.5 (235)	+15.9 (218)	E
7	*d*-Tartaric anhydride 2,3-	(+)	+17.4 (232)	[216][f]	H–D
8	Tetrahydrotaxinine 9,10-[6]		[−5.7 (350)	+49.8 (266)][h]	
		(−)	−17.6 (234)	+8.5 (222)	E
9	Rishitin 2,3- (M)[i]	(−)	−17.6 (235)	+6.1 (218)	E
10	β-Methyl-D-riboside 2,3-	(+)	+9.3 (235)	[210][f]	E
11	α-Methyl-D-riboside 2,3-	(−)	−10.6 (234)	+3.5 (217)	E
12	Serratriol 21-acetate 3,24- (T)[j]	(+)	+14.9 (236)	−10.8 (212)	E–D
13	Hederagenin derivative 3,23- (T)[k]	(+)	+14.0 (233)	−1.9 (219)	E

[a] Positions of the benzoyloxy groups follow compound name. [b] Samples received from: (W), Dr. T. Wada, Teikoku Hormone Co.; (M), Professor T. Masamune, Hokkaido University; (T), Dr. Y. Tsuda, Showa College of Pharmacy. [c] CD spectra were measured using a Jasco ORD/UV-5 spectropolarimeter with CD attachment. [d] E, ethanol; H, *n*-hexane; E–D, ethanol–dioxane (9:1); M–D, methanol–dioxane (9:1); H–D, *n*-hexane–dioxane (9:1). [e] A positive chirality is predicted for this diaxial α-glycol because of the 1,3-diaxial interaction between the 10-Me and 2β-OBz groups. [f] Positions of second Cotton in CD curves not clear; position of third extremum (shoulder) in ORD curves are given instead. [g] See **1**. [h] Cotton effects due to the enone system. [i] See **2**. [j] See **3**. [k] See **4**.



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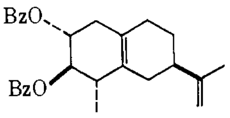

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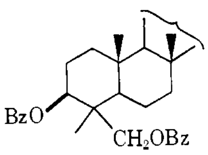

3, β-CH$_2$OBz
4, α-CH$_2$OBz

which is mainly due to the dipole interaction of the benzoate chromophores. This is an extension of the benzoate sector rule,[1,2] which utilized the Cotton effect at 225 mμ (Δε ≈ 3.5) due to the π → π* intramolecular charge-transfer band (230 mμ, ε ≈ 14,000) of the benzoate chromophore. *In glycol dibenzoates having interacting chromophores, the band gives two strong Cotton effects of the same amplitude* (Δε ≈ *9–18*) *but of opposite signs around 233* (*first Cotton*) *and 219 mμ* (*second Cotton*). The splitting indicates that the two Cotton effects are mainly due to a dipole–dipole interaction between electric transition moments of the two benzoate chromophores and that the Cotton effects are separated from each other by a Davydov splitting (Δλ).[3] Figure 1[4] shows ideal summation curves arising from such Davydov splitting.

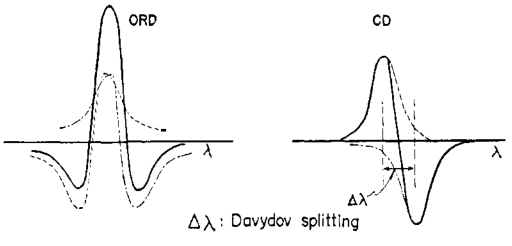

Figure 1. Summation curves (ORD and CD, solid lines) of two Cotton effects (broken lines) of opposite signs separated by Davydov splitting.

If the chiralities of dibenzoates are defined as being positive or negative, respectively, according to whether the rotation is in the sense of a right- or left-handed screw (Figure 2), then *the sign of the first Cotton effect around 233 mμ is in accordance with the chirality* ("*dibenzoate chirality rule*"). This Cotton effect is one of the strongest encountered in common molecules,[5] and its position is fixed at *ca.* 233 mμ. These two aspects make the present rule a convenient method for determining the absolute configurations or chiralities of glycols. Other chromophores usually do not interfere

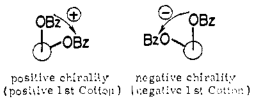

Figure 2. Chiralities of α-glycol dibenzoates.

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

(2) N. Harada and K. Nakanishi, *ibid.*, **90**, 7351 (1968).

(3) A. S. Davydov, "Theory of Molecular Excitons," M. Kasha and M. Oppenheimer, Jr., transl., McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(4) See J. A. Schellman, *Accounts Chem. Res.*, **1**, 144 (1968).

(5) Extremely strong Cotton effects are encountered in 1,1′-bianthryls: see S. F. Mason in "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," G. Snatzke Ed., Heyden, London, 1967, Chapter 4.

because of the difference in position and intensity of the Cotton effects. However, *if necessary, the benzoate Cotton effects can be shifted by introducing suitable para substituents* (entry 4b in Table I, and ref 2).

A typical example of a complex molecule is the derivative of ponasterone A (a phytoecdysone)[6] (entry 6) in which the Cotton effect of the enone group is weaker than that of the dibenzoate and the Cotton effects due to the 2β,3β-dibenzoate moiety are clearly observed. In tetrahydrotaxinine 9,10-dibenzoate (entry 8 and Figure 3),[7] the enone group shows an abnormally strong π → π* Cotton effect at 266 mμ (and a weaker n → π* Cotton effect at 350 mμ), but the dibenzoate Cotton effect is again clearly measurable. The absolute configuration of rishitin[8] is determined as depicted in 2 on the basis of this rule (entry 9). The conformations of the five-membered ring in the anomeric riboside dibenzoates are defined from the chiralities and are shown to be different (entries 10 and 11).

The present treatment is not confined to α-glycols as far as the two benzoate chromophores mutually interact to give a first Cotton effect shifted from that of noninteracting benzoates, *e.g.*, at 233 mμ instead of 225 mμ.[1] Thus in the cholestane 3β,6β-diol derivative (1,4-dibenzoate, entry 5) the Cotton effect sign is in agreement with prediction. The glycol may also include primary alcohols; namely, the sign in the serratriol[9] and hederagenin derivatives[9] (entries 12 and 13) agree with the chirality predicted from the preferred conformation of the 1,3-dibenzoate moiety.

In the case of two chromophores (1 and 2), the rotational strength, R_{oa}, of the transition Ψ_o $(=\varphi_{1o}\varphi_{2o})$ $\rightarrow \Psi_a$ $[=(1/\sqrt{2})(\varphi_{1a}\varphi_{2o} \pm \varphi_{1o}\varphi_{2a})]$ can be for mulated as follows[10] according to the zero-order approximation of the molecular exciton theory

$$R_{oa} = (1/2)\mathrm{Im}[(\boldsymbol{\mu}_{1oa} \pm \boldsymbol{\mu}_{2oa})\cdot(\mathbf{m}_{1ao} \pm \mathbf{m}_{2ao})] \mp (1/2)\pi\bar{\nu}_a\mathbf{R}_{12}\cdot(\boldsymbol{\mu}_{1oa}\boldsymbol{\mu}_{2oa}) \quad (1)$$

where the signs correspond to those of the wave functions, respectively. In the case of the dibenzoate, the magnetic transition moments $\mathbf{m}_{1ao}$ and $\mathbf{m}_{2ao}$ are almost zero because the 230-mμ band is the π → π* transition. Hence the second term, the so-called dipole–dipole interaction term, makes a dominant contribution. Since the 230-mμ intramolecular charge-transfer transition has a long-axis transition moment, the electric transition moments $\boldsymbol{\mu}_{1oa}$ and $\boldsymbol{\mu}_{2oa}$ are approximately parallel to the C–O bonds of alcohols irrespective of the rotational conformation around the C–O bond. (This is of practical value as *application of the present treatment does not necessitate consideration of the benzoyloxy conformation*, *i.e.*, to a first approximation, *only the chiralities of the two C–O bonds need be considered.*) The second term, or the rotational strength R_{oa}, therefore, depends on the chirality of the glycol. In fact, the absolute sign obtained from a theoretical calculation is in accordance with the experimental sign.

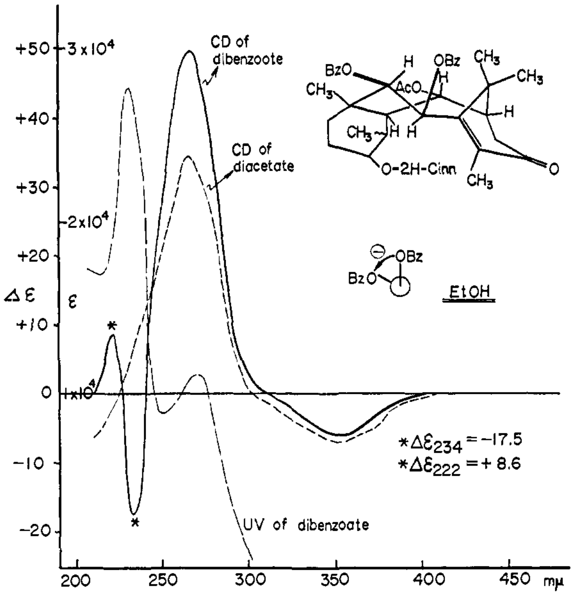

Figure 3. Tetrahydrotaxinine 9,10-dibenzoate.[7] The dibenzoate Cotton effects marked by *; —, CD of dibenzoate; - - - - - -, CD of diacetate; and — — —, uv of dibenzoate.

The second CD Cotton effect is not clear in some dibenzoates (entries 3, 7, and 10). This may be due to instrumental limitations or a strong background ellipticity arising from the extremely strong benzoate absorption at *ca.* 195 mμ (ε ≈40,000); or it may suggest that the first term in eq 1 and/or a higher order perturbation term is making an additional contribution to the Cotton effect. However, this does not detract from the usefulness of the present treatment because the first CD Cotton effects are clearly observable at the usual wavelength around 233 mμ. Extensions of the present treatment to other aromatic systems and tribenzoates will be reported shortly.[11]

Acknowledgments. We are grateful to Mr. M. Ohmori and Drs. Y. Nakadaira and M. C. Woods for preliminary studies on acetonides and related α-glycol derivatives, and to Drs. T. Wada, T. Masamune, and Y. Tsuda for generous gifts of samples listed in Table I.

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(8) N. Katsui, A. Murai, M. Takasugi, K. Imaizumi, T. Masamune, and K. Tomiyama, *Chem. Commun.*, 43 (1968).

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(11) This work has been supported in part by the National Institutes of Health, Public Health Service Research Grant No. CA 08394.

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Photochemical Oxidation of Nitrogenammineruthenium(II) Compounds

Sir:

There is considerable current interest in the nitrogenammineruthenium(II) compounds as possible models for biological nitrogen reduction.[1–4] It was originally

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(1) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).

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(3) D. E. Harrison and H. Taube, *ibid.*, **89**, 5706 (1967).

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