

Table II. Exo:Endo Rate Ratios as a Function of Increasing Electron Demand

	Exo/Endo Rate Ratio		
	k_1^6/k_1^5	k_1^4/k_1^3	k_1^2/k_1^1
<i>p</i> -CH ₃ O	284	312	354
<i>p</i> -H	127	202	1260
<i>p</i> -CF ₃	187	283	6700

Table III. Products of the Solvolysis of the 2-Aryl-5-methyl-2-norbornenyl *p*-Nitrobenzoates

Compound solvolyzed (1, 2)	Products, %	
	7	8
<i>p</i> -CH ₃ O (exo or endo)	75 ± 3	25 ± 3
<i>p</i> -H (exo or endo)	18 ± 3	82 ± 3
<i>p</i> -CF ₃ (endo)	<2	>98

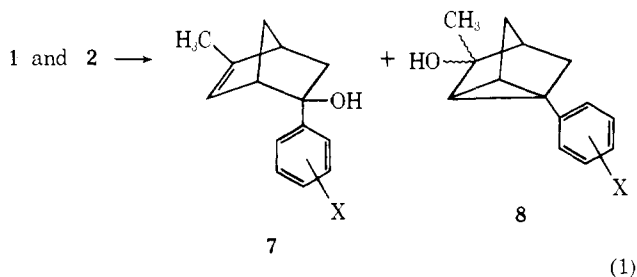
The introduction of a methyl group on a double bond greatly increases its ability to participate by relatively small factors.⁷ Accordingly, we undertook to synthesize **1** by the addition of the appropriate Grignard to 5-methyl-2-norbornenone⁸ and **2** from the hydrolysis products of an appropriate derivative of **1**. Unfortunately, as described later, the alcohol corresponding to **2-p**-CF₃ could not be obtained by this procedure. However, all of these derivatives follow the log (k/k_H) = $\rho\sigma^+$ relationship⁹ closely. Consequently, this relationship was utilized to calculate the rate for **2-p**-CF₃. The rate data are summarized in Table I.

The 5-CH₃ substituent has practically no effect upon the rates of the endo isomers. Thus k_1^3/k_1^1 is 1.05 for *p*-CH₃O, 1.21 for *p*-H, and 0.93 for *p*-CF₃. On the other hand, the 5-CH₃ substituent enhances the rates of the exo isomer, with the enhancement increasing with increasing electron demand: $k_1^4/k_1^2 = 1.19$ for *p*-CH₃O, 7.4 for *p*-H, and 26 for *p*-CF₃.

The effect of the 5-CH₃ is also indicated by the ρ values: **3**, -4.17; **1**, -4.19; **4**, -4.21; **2**, -3.28.

The exo:endo rate ratio has long been the standard criterion to estimate participation. The summary of the data in Table II clearly reveals in the present system an increase in the exo:endo rate ratio with increasing electron demand by the 2-aryl substituent and the absence of the effect in the 2-aryl-2-norbornenyl¹ and 2-aryl-2-norbornyl systems.⁵

The products produced in the solvolysis of the **1** and **2** derivatives in aqueous acetone containing 10 mol % excess sodium acetate were determined by nmr examination (eq 1).



The results (Table III) clearly correspond to the effect anticipated for increasing participation of the double bond with increasing electron demand of the 2-aryl group.

In the case of the 2-aryl-2-norbornenyl *p*-nitrobenzoates¹ (**3**, **4**), not only does the exo:endo rate ratio fail to reflect any influence of increasing electron demand (Table II) but the predominant solvolysis product, in all three cases, is the corresponding 2-aryl-*exo*-norbornenol.¹ This contrasts with the behavior of the 5-CH₃ derivatives. Here, only the *p*-CH₃O derivative yields the *exo* alcohol as the major product. The other derivatives, involving greater electron de-

mand, yield chiefly the rearranged product, 1-aryl-3-methyl-3-nortricyclanol, resulting from a homoallylic rearrangement.

In conclusion, the present study reveals that the tool of increasing electron demand is capable of responding to and detecting relatively small participations. The failure of this tool to detect any measurable electronic contributions in the 2-aryl-2-norbornyl (**5** and **6**) and the 2-aryl-2-norbornenyl (**3** and **4**) systems supports the conclusion that the high exo:endo rate ratios observed in these systems must be the result of other than electronic factors, presumably steric.¹⁰ On this basis, the exo:endo rate ratio of 6700 observed for **2-p**-CF₃/**1-p**-CF₃ would be made up of a factor of approximately 25 representing π participation and one of approximately 270 representing the steric factor.

References and Notes

- (1) E. N. Peters and H. C. Brown, *J. Amer. Chem. Soc.*, **95**, 2398 (1973).
- (2) P. G. Gassman and A. F. Fentiman, Jr., *J. Amer. Chem. Soc.*, **92**, 2549 (1970).
- (3) E. N. Peters and H. C. Brown, *J. Amer. Chem. Soc.*, **95**, 2397 (1973).
- (4) E. N. Peters and H. C. Brown, *J. Amer. Chem. Soc.*, in press.
- (5) H. C. Brown and K. Takeuchi, *J. Amer. Chem. Soc.*, **90**, 2791, 2793 (1968).
- (6) G. D. Sargent in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1972, Chapter 24, p 1173.
- (7) P. D. Bartlett and G. D. Sargent, *J. Amer. Chem. Soc.*, **87**, 1297 (1965); P. G. Gassman and D. S. Patton, *ibid.*, **91**, 2160 (1969); R. A. Snee, *ibid.*, **80**, 3982 (1958).
- (8) S. E. Masar and H. Krieger, *Suom. Kemistilehti B*, **42**, 1 (1969).
- (9) H. C. Brown and Y. Okamoto, *J. Org. Chem.*, **22**, 485 (1957).
- (10) H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N.Y., 1972, Chapter 11.

Herbert C. Brown,* M. Ravindranathan, Edward N. Peters

Richard B. Wetherill Laboratory, Purdue University
West Lafayette, Indiana 47907

Received June 27, 1974

Long Range Effect in the Exciton Chirality Method

Sir:

The method for determining the absolute configuration of organic compounds from coupled Cotton effects, *e.g.*, exciton chirality method,^{1,2} is theoretically well grounded and nonempirical.^{1,3} From a practical viewpoint it is important to clarify the relation between the observed $\Delta\epsilon$ of split Cotton effects and the geometrical factors which affect these values, especially the distance dependency.^{4,5}

The following data for a series of steroidal glycol dibenzoates show excellent agreement between experimental and theoretical values. In particular the strong interaction still operating between the 3 β - and 15 β -benzoate functions in the D-homo-steroidal 1,8-glycol⁶ **10** (Table I), which was prepared in order to avoid complications arising from a flexible five-membered D-ring, is noteworthy as it shows that the exciton chirality method can be applied to configurational studies of molecules containing quite remote groups. In **10** the distance is *ca.* 12.8 Å but the $\Delta\epsilon$ is still more than ten times stronger than ordinary carbonyl n,π^* Cotton effects. Although the present communication is for dibenzoate systems,⁷ the same treatment should hold for interactions between other chromophores, *e.g.*, enone-benzoate,^{2,8} and others.¹

The *p*-dimethylaminobenzoxyloxy group was chosen as the chromophore since: (i) the strong uv intensity of its 309-nm intramolecular charge transfer band leads to large amplitudes of the coupled Cotton effects;⁹ (ii) the 309-nm band is well separated from the shorter wavelength band and thus facilitates theoretical treatments.

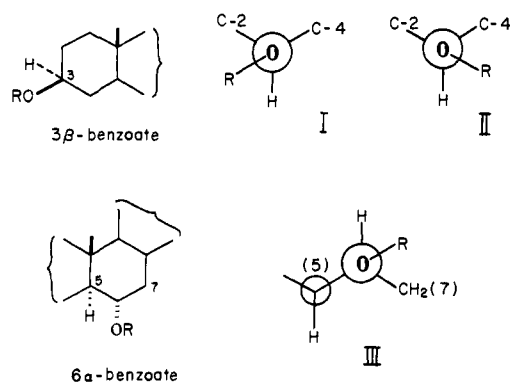
CD curves were calculated on the basis of the point-di-

Table I. Calculated and Observed CD Spectra of Bis(*p*-dimethylaminobenzoates) of Various Steroid Glycols and Interchromophore Distance R_{ij}

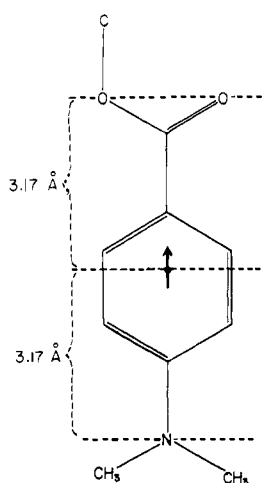
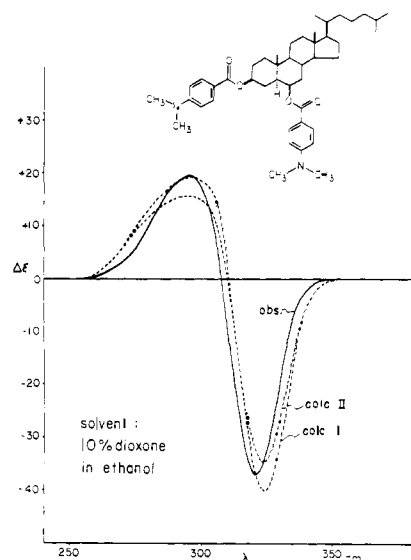
Compd no.	Compound ^a	Chirality	Calcd $\Delta\epsilon^b$ (λ , nm)		Obsd $\Delta\epsilon^c$ (λ , nm)		R_{ij} Å
			1st	2nd	1st	2nd	
1	5 α -Cholestane-2 β ,3 β -	+	+64.0 (323)	-28.5 (296)	+61.7 (320)	-33.2 (295)	8.1
2	5 α -Cholestane-2 α ,3 α -	+	+64.0 (323)	-28.5 (296)	+61.3 (321)	-27.1 (295)	8.1
3	Cholest-5-ene-3 β ,4 β -	-	-64.0 (323)	+28.5 (296)	-57.8 (321)	+35.6 (295)	8.1
4	5 α -Cholestane-3 β ,6 β -	-	-37.2 (323)	+17.3 (295)	-37.6 (320)	+19.2 (295)	9.9
5	5 α -Cholestane-3 β ,6 α -	+	+44.3 (323)	-20.2 (295)	+59.2 (319)	-30.2 (294)	9.5
6	5 α -Cholestane-3 β ,7 α -	+	+29.5 (323)	-13.5 (295)	+28.5 (320)	-11.3 (295)	10.6
7	5 α -Cholestane-3 β ,7 β -	0 ^d	-2.6 (323)	+1.2 (295)	-2.8 (321)	+4.3 (300)	12.4
8	5 α -Androstane-3 β ,11 β -	+	+15.0 (323)	-6.8 (295)	+18.8 (320)	-8.7 (294)	11.4
9	5 α -Pregnane-3 β ,11 α - ^e	-	-21.9 (323)	+10.2 (295)	-35.0 (320)	+17.7 (295)	10.3
10	5 α -D-Homoandrostane-3 β ,15 β -	-	-13.9 (323)	+6.5 (295)	-20.4 (319)	+6.0 (291)	12.8

^a Positions of *p*-dimethylaminobenzyloxy groups follow compound name. ^b Average value of two rotational conformers around 3 β -C-O bond, I and II, excepting entries 1, 2, and 3. ^c Solvent: 10, 20, and 10% dioxane-ethanol for 4, 5, and 6, respectively, ethanol for all others. ^d The calculated and observed values are both *weak* but nevertheless nonzero although the C(3)-O and C(7)-O bonds are parallel. Interestingly, the calculated value for conformer II of the 3-benzoate is zero but that for conformer I is negative. ^e We are grateful to Professor G. Spiteller, University of Göttingen, for the sample of 5 α -pregnan-3 β ,11 α -diol-20-one.

pole geometry,⁶ which was taken as lying on the chromophore long axis (direction of the 309-nm electric transition moment) and at the midpoint between the N and O-O distance (Figure 1).¹⁰



The distances between the point dipoles of the two benzoates, excepting the vicinal dibenzoates 1-3, were taken as follows. Two conformations I and II were assumed for the 3 β -benzoate group which is flanked by two methylene groups. For the other benzoate groups adjacent to ring junctions, *e.g.*, 6 α -benzoate, only one conformation in which the benzoate is trans to the ring junction C-H (III) was considered. The distances and angles of point-dipoles were then computed by assuming regular chair conformations for all six-membered rings. Thus two curves (Figure

**Figure 1.** Point dipole of the *p*-dimethylaminobenzyloxy chromophore.**Figure 2.** Calculated and observed CD curves of 5 α -cholestan-3 β ,6 β -diol bis(*p*-dimethylaminobenzoate). The actual calculated $\Delta\epsilon$ values in Table I were obtained by averaging the calcd I and calcd II curves.

2) corresponding to conformations I and II of the 3-benzoate group were computed; the calculated $\Delta\epsilon$'s shown in Table I are the average of these two values. For vicinal dibenzoates 1-3, it was assumed that both benzoates adopted a single conformation in which they were pointed away from each other; accordingly, only one CD curve was calculated for these.

It has frequently been observed^{2,11} that the intensities of the two split Cotton effects are uneven (Figure 2), the first CD extremum at longer wavelength being sharper and stronger than the second. If a Gaussian distribution is approximated for the component CD curves, the calculated split CD Cotton effects obtained from the two component CD curves are necessarily of equal intensity. However, if the shape of the actual uv curve is simulated for the component CD curves instead,¹² then we find an excellent agreement between observed and computed spectra (Figure 2, Table I).

The data described above show that the exciton chirality method can be employed for absolute or relative configurational studies of compounds containing remote chromophores.¹³

References and Notes

- (1) N. Harada and K. Nakanishi, *Accounts Chem. Res.*, **5**, 257 (1972), and references therein.
- (2) M. Koreeda, N. Harada, and K. Nakanishi, *J. Amer. Chem. Soc.*, **96**,

266 (1974).

- (3) R. Grinter and S. F. Mason, *Trans. Faraday Soc.*, **60**, 274 (1964).
 (4) The CD curve of a binary system consisting of the same two chromophores can be formulated as follows on the basis of the exciton coupling mechanism and a Gaussian distribution for the component CD Cotton effects

$$\Delta\epsilon(\sigma) = \frac{2\sqrt{\pi}\sigma_0^2}{2.296 \times 10^{-38} \Delta\sigma^2} \left(\frac{\sigma_0 - \sigma}{\Delta\sigma} \right) \times \exp \left\{ - \left(\frac{\sigma_0 - \sigma}{\Delta\sigma} \right)^2 \right\} \vec{R}_{ij} \cdot (\vec{\mu}_{10a} \times \vec{\mu}_{j0a}) V_{ij}$$

where σ_0 is excitation frequency of the uv chromophore, $\Delta\sigma$ is standard deviation of Gaussian distribution, R_{ij} is interchromophoric distance, and V_{ij} is interaction energy (cm^{-1}). This shows that the exciton chirality of the system including its sign and amplitude, is essentially definable by the term $R_{ij}(\vec{\mu}_{10a} \times \vec{\mu}_{j0a})V_{ij}$. Furthermore, since V_{ij} is proportional to R_{ij}^{-3} , the amplitude $\Delta\epsilon$ is proportional to R_{ij}^{-2} , provided the interchromophoric angle remains unchanged.⁶

- (5) Computation of the dihedral angle dependency of $\Delta\epsilon$ of a vicinal dibenzoate shows that it resembles a sine curve with its maximum value at ca. 70° and zero values at 0 and 180° .⁶
 (6) Details of experiments and calculations will be published.
 (7) N. Harada, and K. Nakanishi, *J. Amer. Chem. Soc.*, **91**, 3989 (1969).
 (8) It has been shown that coupling exists between steroidal 4-en-3-one moieties and 17-benzoate groups; V. Delaroff and R. Viennet, *Bull. Soc. Chim. Fr.*, 277 (1972).
 (9) N. Harada, S. Suzuki, H. Uda, and K. Nakanishi, *J. Amer. Chem. Soc.*, **93**, 5577 (1971).
 (10) The bond distances and angles are averaged values of recent X-ray crystallographic data: L. L. Reed and J. P. Schaefer, *Acta Crystallogr., Sect. B*, **29**, 1866 (1973); S. K. Arora, M. Sundaralingam, J. S. Dancz, R. H. Stamford, and R. E. Marsh, *ibid.*, 1849 (1973); P. C. Riche, *ibid.*, 2154 (1973); E. E. Castellano and O. J. R. Hodder, *ibid.*, 2566 (1973).
 (11) G. Gotarelli, S. F. Mason, and G. Torre, *J. Chem. Soc. B*, 1349 (1970).
 (12) The shorter wavelength side of a uv band is usually broader than the longer wavelength side (Figure 2); the summation of curves of this type yields a sharp first Cotton effect and broader second Cotton effect.
 (13) Supported by NSF GP 40087.
 (14) On leave of absence from Chemical Research Institute of Nonaqueous Solutions, Tohoku University, Sendai, 980, Japan.

Sow-mei Lai Chen, Nobuyuki Harada,¹⁴ Koji Nakanishi*

Department of Chemistry, Columbia University
 New York, New York 10027

Received August 24, 1974

Nuclear Magnetic Resonance Study of Stereospecific Dimerization of Dicyanohemin

Sir:

The significance of "donor-acceptor" as distinct from hydrophobic interaction in porphyrin-protein linkages in hemoproteins is now widely recognized¹⁻⁴ on the basis of a variety of physical and chemical evidence. The propensity for porphyrins to participate in π interactions is evidenced both in their interaction with organic donor and acceptors,^{5,6} and by their tendency to dimerize or aggregate in solution.⁷⁻¹⁰

The structure of previously reported⁷⁻¹⁰ "loose" porphyrin dimers, characterized by their concentration-dependent intermolecular ring current shifts, is thought to consist of a parallel orientation of the two porphyrin planes with an estimated separation of 8–10 Å, whether or not a metal^{8,10} or small axial ligand¹⁰ is present. Minor preferences for orientation of the porphyrin planes have been attributed to either dipole interactions⁷ or steric effects.¹⁰ Only in the related magnesium chlorophyll-type system¹¹ has significant stereospecificity in the dimerization been detected, where it was shown to arise from intermolecular coordination involving basic peripheral substituents. In no porphyrin systems to date has any evidence been found for a "tight" dimer with separations corresponding to distances found in donor-acceptor complexes¹² or hemoproteins.^{1,4}

We report here on a proton nmr relaxation study of the dimerization of dicyanohemin,¹³ (C in Figure 1), in methanol-*d*₄ which reveals a "tight" dimer with planar spacing of

<4.5 Å that reflects a high degree of stereospecificity in the donor-acceptor interaction.

The "tight" dimer was characterized by the highly stereospecific intermolecular paramagnetic relaxation¹⁴ observed at low temperature. Proton ftmr traces¹⁵ of the four recently assigned¹³ methyl and the two vinyl α -protons are illustrated in A and B of Figure 1 for 0.005 and 0.05 M solutions at -80° . At low concentration, the four methyl line widths (and two vinyl) are approximately the same, as observed at 25° at all concentrations. At -80° , the 1-CH₃ and 8-CH₃ methyls broaden selectively with increasing hemin concentration; the 3-CH₃ and 5-CH₃ are affected very little. Similarly, one vinyl α -H is also broadened. This paramagnetic relaxation (primarily dipolar¹⁴ in origin) is independent of field,¹⁶ and must therefore arise from intermolecular dipolar relaxation of the methyl protons in one porphyrin by the iron of the other porphyrins in the dimer.

The concentration dependence of the line widths suggests that a single type of species exists in solution, whose structure reflects stereospecific interaction involving predominantly pyrroles I and IV. An estimate of the separation of the porphyrin planes in the dimer¹⁷ can be made on the basis of the relative importance of inter- vs. intramolecular paramagnetic dipolar relaxation for the methyl groups. At the lowest temperature where the two low-field resonances can be resolved, (ca. -95°) the 8-CH₃ line width is ~60–80% greater than the 5-CH₃ line width. This requires that in the dimer, [P^IFe^I(CN)₂]⁻–[P^{II}Fe^{II}(CN)₂]⁻, the 8-CH₃ of P^I is about as close to Fe^{II} as to Fe^I, ($r(\text{Fe}^{\text{I}}-8\text{-CH}_3^{\text{I}}) \approx 5.6$ Å). The proposed structure consistent with this distance is depicted in D in Figure 1. Consideration of the steric interaction between 8-CH₃ and CN⁻ (1-CH₃ and CN⁻) leads to an estimated interplane separation of <4.5 Å, which is

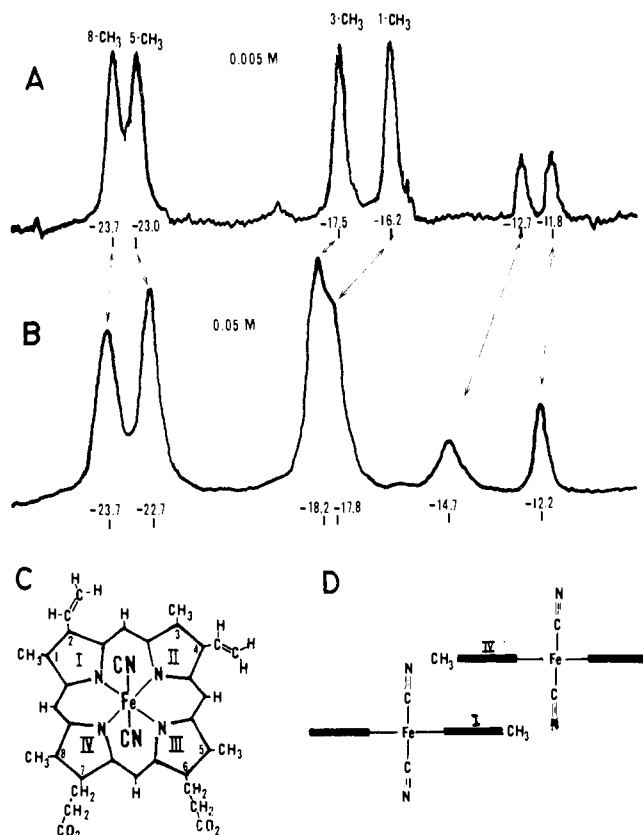


Figure 1. Proton ftmr traces of (A) 0.005 M and (B) 0.05 M solutions of dicyanohemin (protoporphyrin IX ferric dicyanide), in methanol-*d*₄ at -80° . C represents the structure of dicyanohemin and D the configuration of the proposed dimer.