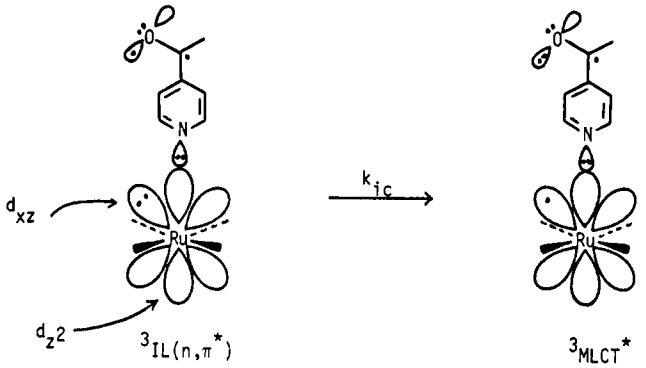
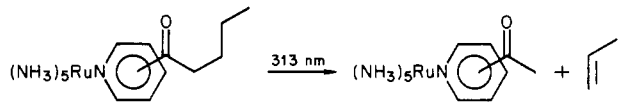
Scheme II




the photokinetic results. Since the ligand could not be displaced thermally from the complex, olefin formation was monitored by GC analysis. The reaction was quenched by conjugated dienes. Slopes of linear Stern-Volmer plots[13] and the triplet lifetimes calculated therefrom[14] are also listed in Table I. No other volatile products were obtained from the para complexes; free ligand, but no acetylpyridine, was formed in low quantum yields from the meta complexes. This selective displacement is consistent with Ford's observations.[8] The complete lack of acetylpyridine formation from any of the complexes indicates that all of the type II reactions come from complexed acylpyridine.




Comparable data were obtained for the acylpyridine hydrochlorides, chosen as the best available model for the complexed ligands.[4] Table I compares the parallel behavior of the protonated and complexed acylpyridines. When the observed quantum yields for the complexes are corrected for only partial absorption by ligand, the complexes and salts are seen to have comparable quantum yields. In each case, quantum yields are low but independent both of $\gamma$ C-H bond strength and of triplet lifetime. Such behavior proves that triplet lifetimes are determined solely by rates of $\gamma$-hydrogen abstraction.[15] The facts that ligand quantum yields are independent of triplet reactivity and equal to those in the uncomplexed ligands indicate that internal conversion from the triplet IL to the lower lying MLCT states does not compete with triplet ligand reaction. Therefore we can conclude that *the rate of internal conversion ($k_{ic}$) in these complexes is less than $10^8$ $s^{-1}$.*

So few $k_{ic}$ values are known that it is difficult to discuss the relatively low value for these complexes. Liu concluded that $k_{ic}$ for $T_2$ ($E_T$ = 74 kcal) to $T_1$ ($E_T$ = 43 kcal) in several anthracenes is $\sim 5 \times 10^9$ $s^{-1}$.[16] The value for $S_2$ (81 kcal) to $S_1$ (41 kcal) in azulene is $10^9$ $s^{-1}$.[17] These transitions are relatively slow because of large energy gaps, even though the $\pi,\pi^*$ excited states occupy the same space. The energy gaps in the complexes are comparable or smaller; $E_T(n,\pi^*)$ = 71-73 kcal and $E_T$(MLCT) = 40-50 kcal.[18] The much lower value of $k_{ic}$ must then reflect poor orbital overlap. The MLCT transition is primarily a d-$\pi^*$ transition, and the lowest $\pi^*$ orbital in phenyl ketones is localized largely on the carbonyl.[2b] Therefore, $k_{ic}$ really measures a $d_{xz}$-$n_O$ electron demotion as shown in Scheme II. Although the CO and Ru centers are not very far apart, the coplanar n and $d_{xz}$ orbitals are highly directed and almost perpendicular to each other. Therefore both poor orientation and the intervening nuclei of the pyridine ring combine to minimize orbital overlap.

The fact that absorption-corrected quantum yields for the Ru-complexed acylpyridines are comparable to those for the simple protonated acylpyridines indicates that internal conversion from *singlet* ligand $n,\pi^*$ to MLCT state does not compete significantly with ligand intersystem crossing. Such intersystem crossing is very rapid ($k > 10^{10}$ $s^{-1}$).[19] The low quantum yields from these positively charged acylpyridines indicate that the 1,4-biradical intermediates revert to ground-state ketones much more efficiently than usual,[20] behavior which we do not fully understand.

The actual $k_r$ values for the complexed acylpyridine triplets are half those of the protonated ketones and 2-4 times those of the free acylpyridines.[7b] The correctness of this order depends on $k_q$ being equal for all these types of compounds.[14] The order is reasonable if the variation reflects primarily an inductive effect; the pyridine nitrogen in the complexes is only partially positive, the $Ru^{2+}$ charge being spread over six ligands.

We are currently studying complexes with less reactive acylpyridine ligands to pinpoint $k_{ic}$ values more accurately.

**Acknowledgment.** This work was supported by NSF Grant CHE-76-11892 and CHE-79-10831. R.B.-L. thanks Dow Chemical Co. for a fellowship administered by the MSU Chemistry Department.

(13) (a) Turro, N. J. "Modern Molecular Photochemistry", Benjamin/Cunnings: Menlo Park, CA, 1978; p 246-248. (b) Wagner, P. J., "Creation and Detection of the Excited State"; Lamola, A., Ed.; Marcel Dekker: New York, 1971; Vol IA, p 173.

(14) A bimolecular rate constant of $1 \times 10^{10}$ $M^{-1}$ $s^{-1}$ was assumed for quenching: Giering, L.; Steel, C., private communication. See: Giering, L.; Berger, M.; Steel, C. *J. Am. Chem. Soc.* **1974**, *96*, 953.

(15) (a) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 5896. (b) Wagner, P. J.; Kelso, P. A.; Zepp, R. G. *Ibid.* **1972**, *94*, 7480.

(16) (a) Liu, R. S. H.; Edman, J. R. *J. Am. Chem. Soc.* **1968**, *90*, 213. (b) Campbell, R. O.; Liu, R. S. H. *Ibid.* **1973**, *95*, 6560.

(17) Birks, J. B. *Chem. Phys. Lett.* **1972**, *17*, 370.

(18) Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 2841.

(19) Anderson, R. W.; Hochstrasser, R. M.; Lutz, H.; Scott, G. W. *J. Chem. Phys.* **1974**, *61*, 2500.

(20) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506.

## Reaction of $(CH_3)_3SnM$ and $Ph_3SnM$ (M = Li, Na, K) with Optically Active 2-Octyl Tosylate, Chloride, and Bromide[1]

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*Received March 16, 1981*

Traditionally, investigations of the mechanism of substitution reactions have been greatly aided by stereochemical studies. The application of classical experimental procedures (i.e., polarimetry) to such studies require that the maximum rotation of the product also be known; this fact has prevented the general application of this procedure to the elucidation of most organometallic reaction mechanisms, since the optical resolution of such substances is frequently impractical.[2] Optical resolution becomes unnecessary, however, if the product in question can be synthesized stereospecifically. We report here the stereospecific synthesis of two such mechanistically significant compounds, trimethyl- and triphenyl(2-octyl)tin (**1** and **2**), together with several related findings.

On the basis of our previous observation that the reaction of $(CH_3)_3SnM$ (M = Li, Na, K) with either *cis*- or *trans*-4-*tert*-butylcyclohexyl tosylate proceeds with essentially complete (>99%) *inversion* of configuration,[3] it seemed reasonable to expect that

(1) This work was supported by NSF (Grant 80-17405) and DOE (Contract DE-AS05-80ER-10662).

(2) Alternative procedures have been developed which circumvent this difficulty by employing diastereomeric rather than enantiomeric substrates; however, such techniques are not without their own shortcomings. Cf.: Bock, P. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2826 and references therein.

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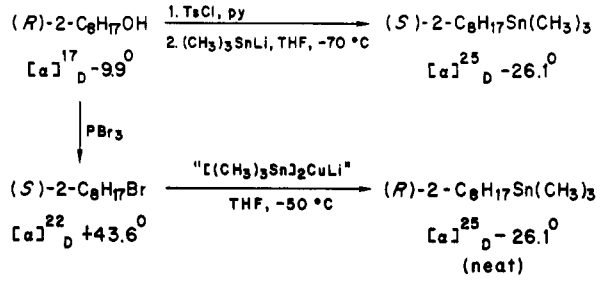
**Table I.** Reaction of $(CH_3)_3SnM$ with Optically Active 2-Octyl Bromide, Chloride, and Tosylate in THF

$$(CH_3)SnM + R^*\text{-}X \xrightarrow[-MX]{} R^*\text{-}Sn(CH_3)_3$$

| R*-X[a] | $[\alpha]^{25}_D$, deg | $CH_3SnM$ (concn, M) | temp, °C | yield, % R*-Sn(CH₃)₃ | obsd $[\alpha]^{25}_D$, deg | corr $[\alpha]^{25}_D$,[b] deg | enantiomeric excess,[c] % |
|---|---|---|---|---|---|---|---|
| | | | Normal Addition[d] | | | | |
| OTs | −8.9[b] | $(CH_3)_3SnLi$ (0.4) | 0 | 74 | +23.0 | +25.6 | 98 |
| | −8.9[b] | | −70 | 4 | +23.5 | 26.1 | 100 |
| Cl | +6.85 | $(CH_3)_3SnLi$ (0.4) | 25 | 51 | −4.32 | −23.5 | 90 |
| | +34.4 | | 0 | 62 | −24.2 | −26.2 | 100 |
| Br | +39.6 | $(CH_3)_3SnLi$ (0.4) | 0 | 69 | −12.6 | −13.9 | 53 |
| | +35.5 | | −70 | 60 | −17.6 | −21.7 | 83 |
| | +35.5 | $(CH_3)_3SnNa$ (0.4) | 0 | 55 | −7.25 | −8.90 | 34 |
| | +35.5 | | −70 | 45 | −13.2 | −16.3 | 62 |
| | | | Inverse Addition[e] | | | | |
| OTs | −8.9[b] | $(CH_3)_3SnLi$ (0.4) | −70 | 7 | +23.0 | 25.6 | 98 |
| Cl | +30.5 | $(CH_3)_3SnNa$ (0.4) | 0 | 52 | −19.9 | −24.3 | 93 |
| Br | +28.4 | $(CH_3)_3SnLi$ (0.4) | 0 | 72 | −16.9 | −25.9 | 99 |
| | +26.6 | $(CH_3)_3SnNa$ (0.4) | 0 | 39 | −15.7 | −25.7 | 98 |
| | +26.6 | $(CH_3)_3SnNa$ (0.1) | 0 | 40 | −15.0 | −26.2 | 100 |

[a] Rotations of optically pure (*S*)-2-halooctane: $[\alpha]^{20}_D$ + 37.3 °(Cl); $[\alpha]^{20}_D$ + 43.4° (Br). See ref 8. [b] This value represents the specific rotation of the corresponding (*R*)-2-octanol. See ref 9. [c] Based on a value of 26.1° for the rotation of optically pure **1**; see text for discussion. [d] Indicates that a solution of R*-X was added to a stirred solution of $(CH_3)_3SnM$. [e] Indicates that a solution of $(CH_3)_3SnM$ was added to a stirred solution on R*-X.

Scheme I




the corresponding reaction with the tosylate of optically active 2-octanol would take place with equivalent stereochemical integrity. Indeed, the reaction of lithium trimethyltin with the tosylate of (*R*)-2-octanol does yield optically active **1**. In an effort to establish the stereospecificity of this reaction, we have carried out an independent but stereochemically equivalent synthesis of **1**. We feel that, taken together, these results (Scheme I) sustain our contention that 26.1° is the rotation of optically pure trimethyl(2-octyl)tin[4] (**1**).

In a parallel study the reaction of lithium triphenyltin with the tosylate of optically active 2-octanol was carried out. The results, summarized below, suggest that optically pure **2** has a rotation of 23.3°.[5]

$$(R)\text{-}2\text{-}C_8H_{17}OH \xrightarrow[2.\ Ph_3SnLi,\ THF,\ 25\ °C]{1.\ TsCl,\ py} (S)\text{-}2\text{-}C_8H_{17}SnPh_3$$
$$[\alpha]^{17}_D\ -9.9° \qquad \mathbf{2},\ [\alpha]^{22}_D\ +23.3°\ (c\ 4.15,\ C_6H_6)$$

The results of the reaction of $(CH_3)_3SnM$ with optically active 2-chloro- and 2-bromooctane are given in Table I. A comparison of these data with those observed in the corresponding reaction of $(CH_3)_3SnM$ with *cis*- and *trans*-4-*tert*-butylcyclohexyl halides[3a] reveals significant similarities. For example, both studies indicate that the influence of the leaving group on reaction stereoselectivity is the same and follows the order OTs > Cl > Br. Temperature, too, has a strong, inverse effect on stereoselectivity in both systems.

One notable difference between these two systems is apparent. Thus, although the reaction of $(CH_3)_3SnM$ with *cis*- and *trans*-4-*tert*-butylcyclohexyl bromide occurs with essentially complete stereochemical equilibration, the corresponding reaction with 2-bromooctane takes place with a stereoselectivity ranging from essentially complete inversion to predominant, but by no means complete, loss of stereochemical integrity.

Two additional consequences of the data in Table I are apparent. First, the mode of reagent addition has a dramatic influence on reaction stereoselectivity. Thus, slow addition of a solution of (*S*)-2-octyl bromide to a well-stirred solution of $(CH_{33}SnNa$ in THF results in substitution with a relatively low degree of stereoselectivity (i.e., 33% net inversion); however, inverse addition (i.e., addition of a solution of $(CH_3)_3SnNa$ to a well-stirred solution of (*S*)-2-octyl bromide in THF) results in a dramatic increase in stereoselectivity. Indeed, it is seen that with only a slight further change in concentration, substitution under inverse addition conditions is actually stereospecific. By comparison, the mode of reagent addition has a much less significant

(3) (a) San Filippo, J., Jr.; Silbermann, J.; Fagan, P. J. *Ibid.* **1978**, *100*, 4834. (b) A trans–cis ratio of 72:28 is observed from the normal addition reaction of $(CH_3)_3SnLi$ with *cis*- and *trans*-4-*tert*-butylcyclohexyl bromide. Inverse addition produces a corresponding value of 64:36. Control experiments were carried out by separately admixing authentic *cis*- and *trans*-(4-*tert*-butylcyclohexyl)trimethyltin with $(CH_3)_3SnLi$. In both instances examination of recovered substrate by GLPC revealed no observed (<1%) isomerism had occurred. Thus, self-exchange, i.e., displacement of $^-Sn(CH_3)_3$ by $(CH_3)_3Sn^-$ does not obtain under these conditions.

(4) For an earlier study of the chemistry of "$[(CH_3)_3sn]_2CuLi$", see: Hudec, J. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1020.

(5) In a pioneering study of the stereochemistry of the reaction of $Ph_3SnM$ with 2-halobutanes, Jensen and Davis,[6] using bond-refraction molecular correlation for stereochemical assignment and relying on accumulated stereoselectivity (including the assumption that bromine cleavage of trineopentyl(2-butyl)tin is stereospecific), concluded that the reaction of $Ph_3SnNa$ with optically active 2-butyl bromide and chloride proceeds with a high degree of stereoselectivity.

(6) Jensen, F. R.; Davis, D. D. *J. Am. Chem. Soc.* **1971**, *93*, 4047.

(7) Kuivila, H. G.; Smith, G. F. *J. Org. Chem.* **1980**, *45*, 2918. Smith, G. F.; Kuivila, H. G.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* **1981**, *103*, 833.

(8) There are several inconsistencies in the literature with respect to the currently accepted values for the rotation of optically pure (neat) 2-chloro- and 2-bromoctane. Some of these values are premised on a value for the rotation of optically pure (neat) 2-octanol of $[\alpha]^{20}_D$ + 8.02°. Two determinations[9,10] of this value suggest that a more accurate value is $[\alpha]^{17}_D$ +9.93°. It is this latter value that we have employed in all our calculations. Three independent investigators have reported the following values for the rotation of purportedly optically pure (−)-2-chlorooctane: $[\alpha]^{20}_D$ −31.6°,[11] $[\alpha]^{20}_D$ −32.4°,[12] $[\alpha]^{22}_D$ −36.15°.[9] In our hands preparation of this material by an alternative procedure[13] yields (−)-2-chlorooctane with a rotation of $[\alpha]^{20}_D$ −37.3°; it is this last value which we have used in calculating the data in Table I. Several values have been reported for the rotation of purportedly optically pure (−)-2-bromooctane: $[\alpha]^{20}_D$ −40.6°,[9] $[\alpha]^{20}_D$ −44.3°,[12] and $[\alpha]^{20}_D$ −43.6°.[11] Preparaton of this material in our hands yield (−)-2-bromooctane with $[\alpha]^{20}_D$ −43.4°. In carrying out the calculations presented in Table I we have employed this last value for the rotation of optically pure (−)-2-bromooctane.

(9) Brauns, D. H. *Recl. Trav. Chim. Pays-Bas* **1946**, *65*, 799.

(10) Kenyon, J. *Org. Synth.* **1926**, *6*, 68.

(11) Hudson, H. R. *Synthesis* **1969**, 112.

(12) Hoffmann, H. M. R. *J. Chem. Soc.* **1964**, 1249.

(13) San Filippo, J.; Romano, L. J. *J. Org. Chem.* **1975**, *40*, 1514.

effect on the stereochemical consequences of the reaction of $(CH_3)_3SnLi$ with a *cis*- or *trans*-4-*tert*-butylcyclohexyl bromide; in fact, stereochemical equilibration still obtains in these reactions; however, a somewhat decreased preference for production of the trans isomer product is observed with inverse addition.[3b]

Second, a comparison of the reaction of $(CH_3)_3SnM$ and $Ph_3SnM$ with optically active 2-octyl bromide reveals that, substitution with $(CH_3)_3SnM$ occurs readily at −20 °C while that with $Ph_3SnM$ exhibits a comparable rate of reaction only when carried out at ambient temperature. However, while the reaction with $(CH_3)_3SnM$ can have a substantial free-radical component depending on various reaction parameters, the corresponding reaction with $Ph_3SnM$, whether carried out by normal or inverse addition, is essentially stereospecific. Thus

$$(S)\text{-}2\text{-}C_8H_{17}Br\ [\alpha]_D +38.6° \xrightarrow[\text{THF, 25 °C}]{Ph_3SnLi} (R)\text{-}\mathbf{2}\ [\alpha]_D -23.3°\ (c\ 4.15, C_6H_6)$$

a significant kinetic distinction exists between free-radical and nonfree-radical pathways in this latter system.

Finally, these findings are relevant to the recently reported study of Kuivila and co-workers[7] who, using inverse addition conditions, concluded that >70% of the yield of **1**, resulting from the reaction of $(CH_3)_3SnNa$ with 2-octyl bromide in THF, is produced by pathways involving nongeminate free-radical combination. By contrast our studies reveal that under equivalent conditions, the reaction of $(CH_3)_3SnNa$ with 2-octyl bromide is highly stereoelective and can even be stereospecific, thereby *excluding* extensive participation of nongeminatge free-radical pathways. As the conclusions of these authors were based on the results of various trapping experiments, we conclude that the additives which were employed as trapping agents must be introducing a substantial perturbation on the mechanism of this reaction and, consequently, that such results cannot be considered as a reliable indication of those mechanisms that obtain in the absence of such reagents.

## A Chiroptical Method for Determining the Absolute Configuration of Allylic Alcohols

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The circular dichroic exciton chirality method, a nonempirical method based on the coupled oscillator theory, has been successfully used in various organic compounds for the determination of absolute configurations.[1] As an extension of the exciton chirality method, we report a new CD method for determining the absolute stereochemistries of allylic alcohols.

The concept of chiral exciton coupling can be extended to nondegenerate systems composed of two different chromophores, e.g., the benzoate/enone system.[2] Allylic alcohol benzoates also give rise to a coupled nondegenerate system. Namely, the benzoate chromophore exhibits an allowed $\pi \rightarrow \pi^*$ intramolecular charge-transfer band at 230 nm, while the C–C double-bond chromophore also shows an allowed $\pi \rightarrow \pi^*$ transition around 195 nm;[3] both $\pi \rightarrow \pi^*$ transitions are polarized along the long axes of the chromophores. Therefore, the exciton theory predicts[4] that, if the two long axes of benzoate and double-bond chromosphores constitute a positive exciton chirality, i.e., right-handed screwness, the first Cotton effect at longer wavelengths (230-nm benzoate Cotton effect) is positive, while the second Cotton effect at shorter wavelengths (195-nm double bond $\pi \rightarrow \pi^*$ Cotton effect) is negative (Figure 1). On the other hand, if the allylic benzoate constitutes a negative exciton chirality, the 230-nm benzoate Cotton effect should be negative.

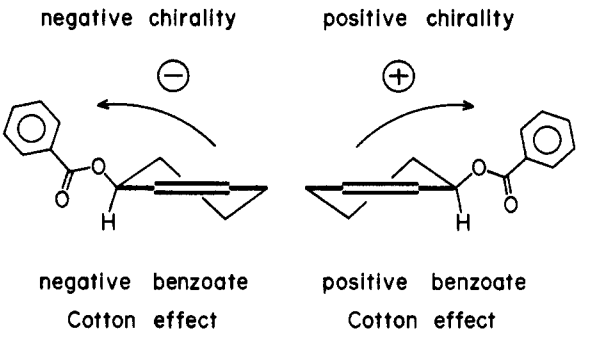


**Figure 1.** Exciton chirality of allylic benzoates and sign of benzoate Cotton effects.

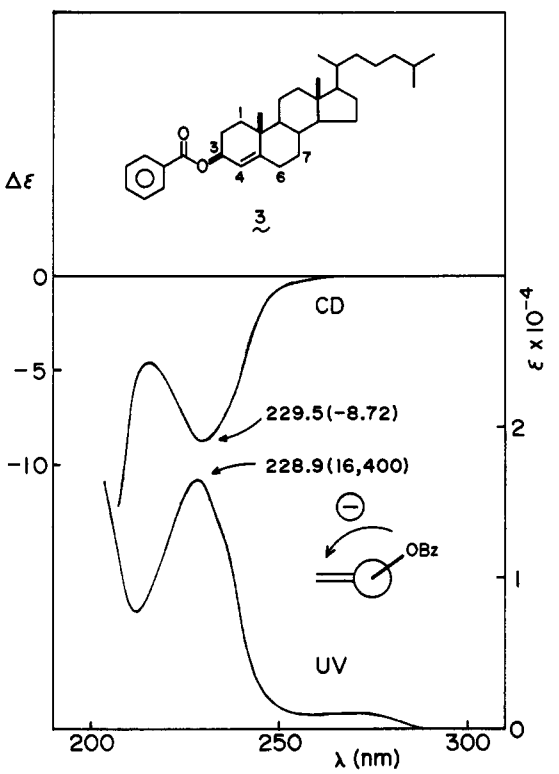


**Figure 2.** CD and UV spectra of chloest-4-en-3β-yl benzoate (**3**) in EtOH.

In addition to the intense $\pi \rightarrow \pi^*$ (or $\pi_x \rightarrow \pi_x^*$) transition, a C–C double-bond chromophore has additional weak $\pi \rightarrow \sigma^*$ and $\pi_x \rightarrow \pi_y^*$ transitions.[5] Moreover, since the olefinic chromophore is also asymmetrically perturbed by allylic substituents[6]

(1) (a) Harada, N.; Nakanishi, K. *Acc. Chem. Res.* **1972**, *5*, 257. (b) Harada, N.; Uda, H. *J. Am. Chem. Soc.* **1978**, *100*, 8022. (c) Harada, N.; Tamai, Y.; Takuma, Y.; Uda, H. *Ibid.* **1980**, *102*, 501 and references cited therein. (d) Harada, N.; Nakanishi, K. "Circular Dichroic Spectroscopy—Exciton Coupling in Organic and Bioorganic Stereochemistry"; University Science Books: Mill Valley, CA, in press.

(2) Koreeda, M.; Harada, N.; Nakanishi, K. *J. Am. Chem. Soc.* **1974**, *96*, 266.

(3) Stich, K.; Rotzler, G.; Reichstein, T. *Helv. Chim. Acta* **1959**, *42*, 1480.

(4) The exciton chirality of nondegenerate systems is theoretically defined by the quadruple product, $\mathbf{R}_{if}(\mu_{i0a} \times \mu_{j0b})V_{ij}$, where $\mathbf{R}_{ij}$ is interchromophoric distance, $\mu_{i0a}$ and $\mu_{j0b}$ are electric transition moments of chromophores $i$ and $j$, respectively, and $V_{ij}$ is interaction energy.

(5) Levin, C. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 3446.

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