and purified on a C_{18} SPE Baker column (3 mL) by using a step gradient (0, 5, 10, 20, 50, and 100%) of CH_3CN in 5 mM ammonium acetate (pH 4.5). The fractions were concentrated in vacuo, freeze–dried, and analyzed by TLC in S_3. C-C-A (8) was removed by elution with 5% CH_3CN and the product was eluted with 20% CH_3CN. The total yield of the deblocking and purification was 28%. The product **10** was chromatographically and electrophoretically uniform and was characterized by alkaline hydrolysis (0.1 N KOH, 100 °C, 20 min) to Cp and A (ratio Cp/A = 2.22); complete digestion with RNAse A (ratio Cp/A = 2.03); complete digestion with snake venom phosphodiesterase (ratio Cp + C/pA = 1.05) and by UV spectra in 0.01 N HCl (λ_{max} = 269 nm; λ_{min} = 236 nm; $A_{250/260}$ = 0.72; $A_{280/260}$ = 1.01; $A_{290/260}$ = 0.69). The product **10** is also identical in several chromatographic and electrophoretic systems with a compound prepared previously by a different approach.[5]

Optically Active Pyrromethenone Amides. Exciton Coupling in Hydrogen-Bonded Dimers

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The amides of xanthobilirubic acid with (*R*)-(+)- and (*S*)-(−)-α-methylbenzylamine (**1** and **2**, respectively) and (*R*)-(+)- and (*S*)-(−)-1-(1-naphthyl)ethylamine (**3** and **4**, respectively) have been synthesized and found to exhibit moderate circular dichroism Cotton effets (CEs) (**1** and **3**: $\Delta\epsilon_{max}^{413}$ −1.3) in dimethyl sulfoxide solvent for the pyrromethenone long-wavelength transitions and stronger bisignate CEs (**1** and **3**: $\Delta\epsilon_{max}^{402} \simeq +3.1$, $\Delta\epsilon_{max}^{446} \simeq +1.3$) in CH_2Cl_2 solvent. The bisignate CE, whose intensity decreases with decreasing pyrromethenone concentration, is assigned to the pyrromethenone–pyrromethenone hydrogen-bonded dimer.

The pyrromethenone chromophore (Figure 1) is found in nature in the bile pigment (4*Z*,15*Z*)-bilirubin IXα, which is the yellow-orange, cytotoxic pigment of jaundice.[1] Pyrromethenones have therefore served as useful adjuncts in studies of jaundice phototherapy and bilirubin structure–biological function relationships.[2] The structures of typical 5*H*-pyrromethenones are known from crystallographic[3,4] studies which show the presence of (1) a lactam tautomer, (2) substantial double bond and single bond character in the C_4–C_5 and C_5–C_6 bonds, respectively, (3) a syn-*Z* configuration C=C at C_4, and (4) essentially planar, dimeric structures with extended pyrrole interplanar angles, $\phi \simeq 4°$.[5] Most of these structural features persist in solution where the H-bonded dimers are in equilibrium with their component monomers in nonpolar solvents (in $CHCl_3$, the association constant, $K_A \simeq 1700$ M^{-1} from vapor phase osmometry studies),[6a] and the monomers exhibit substantially greater twisting ($\phi \simeq 40°$) about C_5–C_6, as deduced from LIS–NMR studies.[6] Additional support for the presence of twisting (calculated $\phi \simeq 33°$) in the monomer and its near absence (calculated $\phi \simeq 5$–$8°$) in the dimer comes from molecular mechanics calculations.[7] These data reveal much about the pyrromethenone pigment and show that in the intermolecularly hydrogen-bonded dimer it is structurally similar to the planar pyrromethenone units found connected as a molecular dimer in the stable, intramolecularly hydrogen-bonded conformer of bilirubin (Figure 2).[9]

Pyrromethenones are typically bright-yellow compounds, possessing a conjugated π-electron system, and they exhibit an intense long-wavelength UV–vis absorption near 400 nm with $\epsilon \simeq 30\,000$. Although they may adopt a dissymmetric (twisted) conformation (Figure 2) and are therefore potentially chiral molecules, the conformational interconversion energy is calculated to be very small, ~1 kcal/mol.[7b] Consequently, their solutions in isotropic media are optically inactive. However, in optically active mesophases, weak circular dichroism (CD) has been detected for the kryptopyrromethenone dimer (Figure 2),[6a,b] but no induced CD (ICD) could be detected for xanthobilirubic acid (XBR, Figure 2) in sodium deoxycholate micelles in pH 7.7–8.0 buffer solution.[10a] Similarly, where heteroassociation, complexation with a chiral solvating agent might be expected, XBR showed no ICD for solutions with β-cyclodextrin;[10b] however, the noncovalent complex with human serum albumin[11] shows a moderately strong ICD.[2d]

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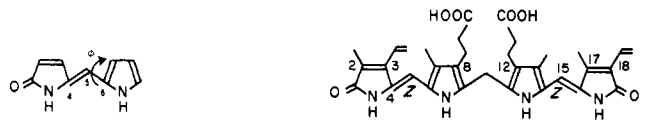


Figure 1. (Left) Pyrromethenone chromophore. (Right) Linear representation of (4*Z*,15*Z*)-bilirubin IXα.

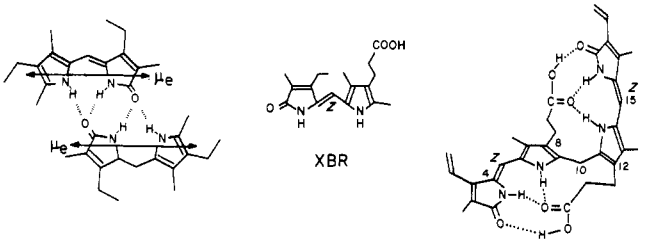
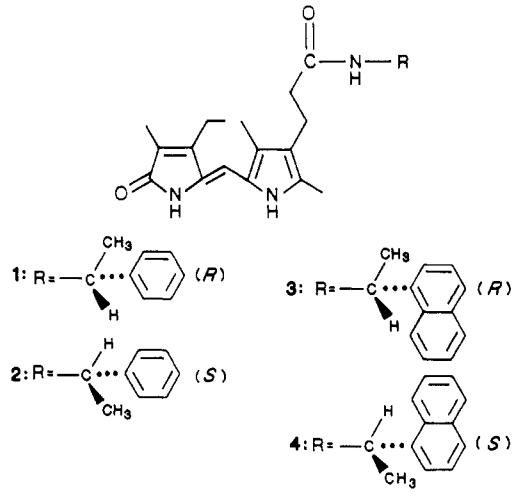


Figure 2. (Left) Intramolecularly hydrogen bonded kryptopyrromethenone, with parallel electric dipole transition moments ($\vec{\mu}_e$). (Middle) Xanthobilirubic acid (XBR). (Right) Folded, intramolecularly hydrogen bonded conformation of (4*Z*,15*Z*)-bilirubin IXα. (Only one of the two conformational enantiomers is shown.)

In order to investigate the relationship between optical activity and structure in pyrromethenones, we synthesized the first amides of XBR with optically active α-methylbenzylamine and 1-(1-naphthyl)ethylamine (**1**–**4**) and examined their CD spectra in solvents that promote dimerization (CH_2Cl_2) and monomerization (DMSO). The results are discussed in terms of exciton coupling theory.



Results and Discussion

Xanthobilirubic acid, prepared as reported previously,[12] was converted to its optically active amide derivatives (**1**–**4**) via the Shioiri[13] procedure by coupling with an optically active amine by using diphenylphosphoryl azide.[12] The amines in this work, (*R*)- and (*S*)-α-methylbenzylamines and (*R*)- and (*S*)-1-(1-naphthyl)ethylamines, were chosen because they are readily available in a state of high optical purity, and the amides they form with XBR have favorable solubility properties.[12]

The CD spectra of amides **1**–**4**, run in dimethyl sulfoxide and shown in Figures 3 and 4, reveal a (−) Cotton effect (CE) for the *R*-configuration amides and a (+) CE of equal magnitude for the *S*-configuration amides—all centered near 413 nm and coinciding well with their intense ($\epsilon \simeq$ 32 000) long-wavelength UV–vis transition near413 nm. The CE magnitudes ($|\Delta\epsilon| \simeq 1.5$) are typical of inherently symmetric (achiral) chromophores perturbed by dissymmetric vicinal action,[14] e.g., (*R*)-2,2-dimethyl-3α-naphthylbutane $\Delta\epsilon_{max}^{280} \simeq -1$ for the ^1L_a transition.[15] Since it is known that pyrromethenone amides are largely monomeric in DMSO[12,16] and that pyrromethenone monomers prefer a twisted (dissymmetric) conformation in solution,[6b] we take the modest $\Delta\epsilon$ values to indicate that the chiral amine perturber has little or no effect on the potential pyrromethenone conformational equilibrium: XBR amide ($\phi \simeq +40°$) $\rightleftarrows$ XBR amide ($\phi \simeq -40°$). Consequently, the observed CEs in DMSO may be understood as originating from dissymmetric perturbation of a (time-average) symmetric (planar) pyrromethenone chromophore. As such, the CD is not different from that seen with aromatic chromophores.[14,15,17]

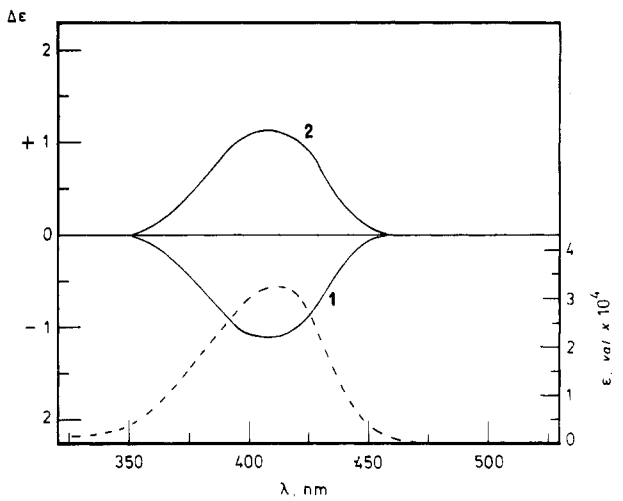


Figure 3. Circular dichroism (—) and UV–vis (- - -) spectra of 4×10^{-5} M solutions of (−)-xanthobilirubic acid (*R*)-α-methylbenzylamide (**1**) and (+)-xanthobilirubic acid (*S*)-α-methylbenzylamide (**2**) in DMSO at 20 °C.

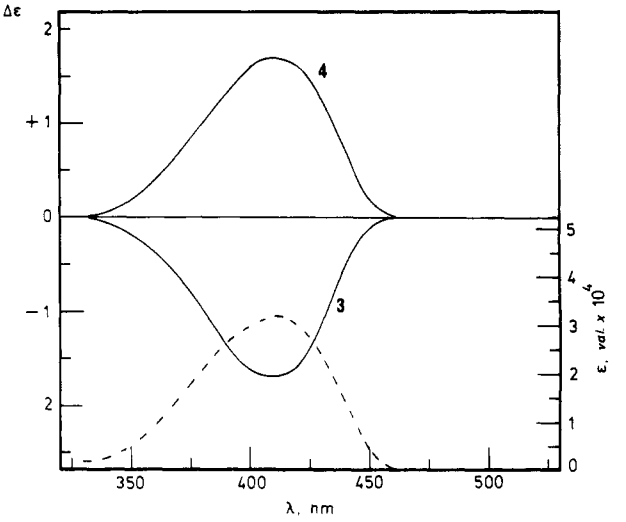


Figure 4. Circular dichroism (—) and UV–vis (- - -) spectra of 4×10^{-5} M solutions of (−)-xanthobilirubic acid (*R*)-1-(1-naphthyl)ethylamide (**3**) and (+)-xanthobilirubic acid (*S*)-1-(1-naphthyl)ethylamide (**4**) in DMSO at 20 °C.

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(14) For leading references, see: Deutsche, C. W.; Lightner D. A.; Woody, R. W.; Moscowitz, A. *Annu. Rev. Phys. Chem.* **1969**, *20*, 407–448.
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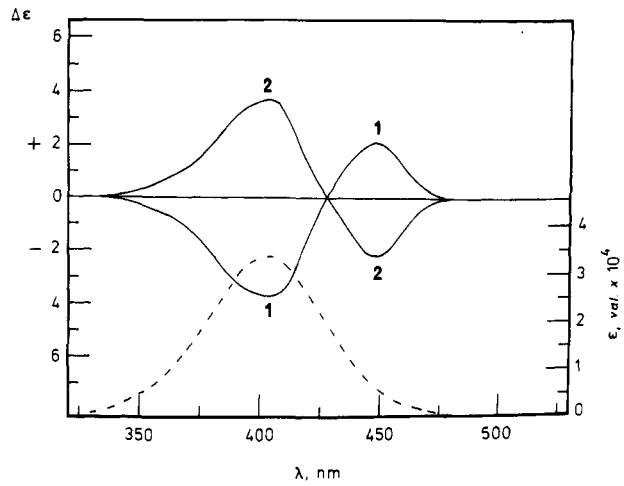

Figure 5. Circular dichroism (—) and UV–vis (- - -) spectra of 4×10^{-5} M solutions of (–)-xanthobilirubic acid (*R*)-α-methylbenzylamide (**1**) and (+)-xanthobilirubic acid (*S*)-α-methylbenzylamide (**2**) in CH_2Cl_2 at 20 °C.

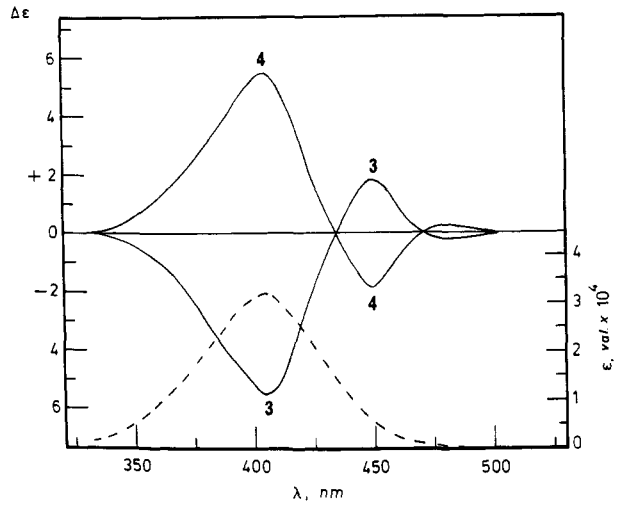

Figure 6. Circular dichroism (—) and UV–vis (- -) spectra of 4×10^{-5} M solutions of (–)-xanthobilirubic acid (*R*)-1-(1-naphthyl)ethylamide (**3**) and (+)-xanthobilirubic acid (*S*)-1-(1-naphthyl)ethylamide (**4**) in CH_2Cl_2 at 20 °C.

The CD data of **1**–**4** in CH_2Cl_2 solvent (Figures 5 and 6) differ significantly from those run in DMSO: the CD curves are bisignate. The *R*-configuration amides show a (–) CE maximum near 405 nm and a weaker (+) CE near 450 nm, and the *S*-configuration amides show a mirror image behavior, with both magnitudes being greater than those seen in DMSO solvent. The presence of a second CD band suggests the presence of a second species in CH_2Cl_2 solvent, one not present in DMSO, viz. the H-bonded dimer (Figure 2).[6a] The observed CD spectrum in CH_2Cl_2 can thus be seen as arising from overlapping CEs from the monomeric and dimeric species, where the dimer CD is inherently bisignate.

Both the intermolecularly hydrogen-bonded pyrromethenone species and bilirubin are pyrromethenone dimers; the former is a double molecule, the latter a covalently linked molecular dimer. As such, both systems are potential molecular exciton systems.[18] The relative orientations of the component chromophores differ vastly,

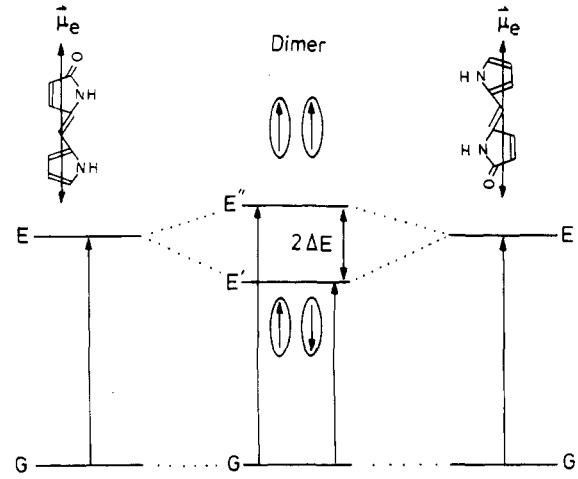

Figure 7. (Upper) Two pyrromethenone chromophores and their long wavelength excitation electric dipole transition moments ($\vec{\mu}_e$). (Lower) State energy levels (G = ground state, E = first electronic excited state) and their exciton interaction to give the pyrromethenone H-bonded dimer electronic excited state showing a Davydov splitting energy of 2ΔE separating the dimer excited states E″ and E′. State E″ corresponds to the in-phase alignment of the transition moments, state E′ to the out-of-phase alignment. In the UV–vis, excitation G → E″ is allowed, the excitation G → E′ is forbidden (see ref 20).

however. The pyrromethenone planes of bilirubin intersect at an angle of ~100°,[9a] but the pyrromethenone units of the intermolecularly H-bonded dimer are assumed to be nearly coplanar.[3,4,6] The molecular exciton system for bilirubin, which adopts enantiomeric conformations (Figure 2), has been discussed previously in connection with its heteroassociation complexes with albumin[2d,19] and cyclodextrins,[10b] but has not been recognized heretofore for pyrromethenones, except when bound in a >1:1 ratio on albumin.[2c,d]

Kasha et al.[20] showed that double molecules with parallel electric dipole transition moments are expected to exhibit exciton splitting (2ΔE) resulting in a blue shift for the electronic transition of the dimer relative to the monomer. The spectral shift arises because electronic excitation from the ground state is allowed only to the (higher energy) exciton state with in-phase orientation of the transition moments: G → E″ allowed and out-of-phase (G → E′) forbidden (Figure 7). Examples may be found in n → π* transitions of van der Waals dimers of dye molecules,[20] helical arrays of hydrogen-bonded base pairs in DNA-like molecules,[14,20,21] and in simple H-bonded dimers, e.g. 7-azaindole.[21] Consequently, one might expect to see a blue shift in the long-wavelength UV–vis band of the XBR amide dimer (in CH_2Cl_2) relative to that of the monomer (in DMSO). The shift will be attenuated somewhat by the fact that at concentrations of $\sim 10^{-4}$ M there is considerable monomer present in equilibrium with dimer, and thus the observed band will be a "summed" band from the two species. If we take an exciton splitting energy of ~2000 cm^{-1}, e.g. that of the 7-azaindole H-bonded dimer, then the allowed (G → E″) UV–vis exciton transition of the dimer will appear near ~400 nm and the forbidden (G → E′) exciton transition at ~430 nm. The UV–vis transition curves arising from the exciton system will be added to the monomer UV–vis, which is centered near ~413 nm (neg-

(17) For leading references see: Charney, E. *The Molecular Basis of Optical Activity*; Wiley: New York, 1979; pp 227–234.
(18) For leading references and examples, see: Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy-Exciton Coupling in Organic Stereochemistry*; University Science Books: Mill Valley, CA, 1983.
(19) Blauer, G.; Wagnière, G. *J. Am. Chem. Soc.* **1975**, *97*, 1949–1954.
(20) For leading references, see: Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371–392.
(21) Kasha, M.; El-Bayoumi, M. A.; Rhodes, W. *J. Chim. Phys. Phys.-Chem. Biol.* **1961**, *58*, 916–925.

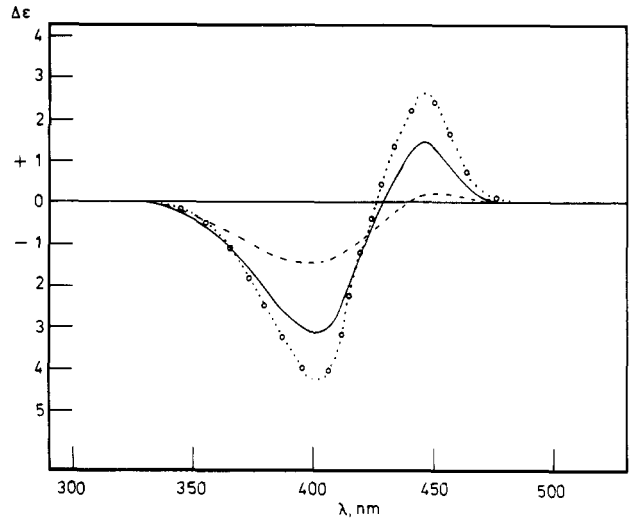

Figure 8. Circular dichroism spectra of 1 in $CHCl_3$ solvent at 20 °C reflecting a 100-fold concentration range. (---) 4×10^{-6} M, (—) 4×10^{-5} M, (o) 4×10^{-4} M.

lecting solvent effects on the monomer transition) to give the observed composite band centered near ~405 nm. Any UV–vis curve due to the forbidden G → E′ transition will add to the long-wavelength wing of the curve and thus broaden this side of the curve (see, e.g., Figure 5) relative to that seen for the monomer (in DMSO, Figure 3).

For each of the UV–vis excitations (Figure 7) originating from monomer (G → E) and dimer (G → E″, G → E′) there will be a corresponding CD transition, which has its origin in the magnetic as well as the electric dipole transition moments, and is thus governed by somewhat different selection rules.[14] The exciton dimer will exhibit oppositely signed CD transitions[10b,20] corresponding to G → E″ and G → E′ whereas the monomer will show the single transition G → E described earlier for solutions in DMSO. However, the observed CD band will be the result of the super position of CD bands coming from both the dimer and the monomer. As such, it will show the general characteristics of a bisignate CD, but with one of the widely separated[22] maxima enhanced in intensity by addition of the monomer CD curve. The resultant CD curve should be concentration and solvent dependent, with larger Δε values coming from solutions where the dimer concentration is increased. Thus, as the concentration of 1 decreases 100-fold in $CHCl_3$, the bisignate CD decreases in intensity and tends to become monosignate in highly dilute solutions (Figure 8), with Δε and λ_{max} values approaching those of 1 in DMSO, where little or no dimer is assumed to be present.[7,12,16]

Bichromophoric exciton CD transitions are generally more intense than the CD transition arising from dissymmetric perturbation of the monochromophore unit.[18] A comparison of Figures 5 and 6 with Figures 3 and 4 show that the CDs of solutions containing dimer tend to be more intense than the monomer CD. The intensity of the exciton CD is related to the relative orientation of the electric dipole transition moments of the coupled chromophores.[18] When they are parallel and lie in the same plane, the rotatory strength values are at a minimum and approach $R = 0$, or $\Delta\epsilon = 0$ for achiral chromophoric units. However, when the interplanar angle is ~90°, the Δε values may become quite large, e.g. Δε ~ 200–300 for bilirubin,[23] or even larger (~1000) for anthracene molecular dimers.[18] The comparatively small Δε values for the pyrromethenone H-bonded dimer suggest a large interplanar angle, one approaching 180° (near coplanarity of the pyrromethenone units).

From the signed order of the exciton bands, one is often able to determine the absolute configuration of the exciton system. For well-defined orientations of the electric dipole transition moments, a (+) longer wavelength CE followed by a (−) shorter wavelength CE is associated with a (+)-chirality or handedness.[18] If the transition moments ($\vec{\mu}_e$) of the dimer lie inclined in the pyrromethenone planes (Figure 7) as calculated,[6a,19] then one is tempted to think that they transcribe a (+) chirality for 1 and 3 and a negative chirality for 2 and 4. However, these conclusions are tenuous at best, given the uncertainties associated with the exact location of the pyrromethenone transition moment and the ~180° interplanar angle.

Summary

Optical activity of the pyrromethenone chromophore can be detected by CD spectroscopy of the amides of XBR prepared from optically active amines. The CDs are monosignate in DMSO solvent, in which the pigment is monomeric, but bisignate in CH_2Cl_2 or $CHCl_3$ solvents, in which the pigment is known to dimerize. The bisignate CD is attributed to the intramolecularly hydrogen bonded dimer, which is a double molecular exciton with both pyrromethenones lying essentially in the same plane. These data may be contrasted with those where the pyrromethenone amides are connected by covalent bonds and held in a folded conformation. Thus, the molecular exciton represented by the bilirubin bis amide of (*R*)-(+)-α-phenethylamine exhibits a much larger bisignate CD [$\Delta\epsilon^{413}_{max} \simeq +25$, $\Delta\epsilon^{466}_{max} \simeq -36$ ($CHCl_3$)].[24] No induced CDs are detected for XBR in DMSO or CH_2Cl_2 in the presence of a larger excess of the optically active amines used in this work.

Experimental Section

General Procedures. Circular dichroism (CD) spectra were recorded on a JASCO J-40 instrument equipped with a photoelastic modulator and a J-DPY data processor or a JASCO J-600 spectropolarimeter. Ultraviolet (UV) spectra were recorded on a Cary 219 spectrophotometer, and rotations were determined in dimethyl sulfoxide, unless otherwise indicated, on a Perkin-Elmer 141 polarimeter. All nuclear magnetic resonance (NMR) spectra were determined in $CDCl_3$ or DMSO-d_6 and are reported in δ (ppm) downfield from tetramethylsilane on a JEOL FX-100 instrument. Infrared (IR) spectra were run on a Perkin-Elmer Model 599 instrument. All melting points are uncorrected and were determined on a Mel-Temp capillary apparatus. Combustion analyses were performed by MicAnal, Tucson, AZ. Spectral data were obtained with spectral grade solvents (MCB): chloroform, methylene chloride, and dimethyl sulfoxide. Other solvents were distilled and dried before use: triethylamine (Aldrich) distilled from CaH_2 under N_2 and stored under N_2; *N*,*N*-dimethylformamide (Aldrich) dried over 4A molecular sieves and distilled at reduced pressure (16 mm). Diphenylphosphoryl azide, (*R*)-(+)-α-methylbenzylamine, $[\alpha]^{23}_{589}$ +39° (neat), and (*S*)-(−)-α-methylbenzylamine, $[\alpha]^{23}_{589}$ −39° (neat), were obtained from Aldrich; (*R*)-(+)-1-(1-naphthyl)ethylamine, $[\alpha]_{589}$ −76° (neat), and (*S*)-(−)-1-(1-naphthyl)ethylamine, $[\alpha]_{580}$ −79° (neat), were obtained from Norse Laboratories. Analytical thin-layer chromatography was accomplished on J. T. Baker silica gel 1B-F plates with

(22) This phenomenon arises from cancellation in the region between the band centers of two oppositely signed CD curves and is shown graphically in: Wellman, K. M.; Lauer, P. H. A.; Briggs, W. S.; Moscowitz, A.; Djerassi, C. *J. Am. Chem. Soc.* **1965**, *87*, 66–72.

(23) For leading references, see: Blauer, G. *Isr. J. Chem.* **1983**, *23*, 201–209.

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$CHCl_3/CH_3OH$ (8:1, v/v) or $CHCl_3$/acetone/CH_3OH (16:3:1, v/v/v) as developing solvents.

(−)-Xanthobilirubic Acid (*R*)-α-Methylbenzylamide (1). Xanthobilirubic acid[12] (181 mg, 0.6 mmol) was dissolved in 50 mL of dry, distilled *N,N*-dimethylformamide. To this solution were added diphenylphosphoryl azide (0.826 g, 3 mmol), triethylamine (160 mg, 1.6 mmol), and (*R*)-(+)-α-methylbenzylamine (160 mg, 1.6 mmol), and (*R*)-(+)-α-methylbenzylamine (145 mg, 1.2 mmol), and the solution was heated for 6–12 h under N_2 at 55–60 °C until the xanthobilirubic acid was consumed (as checked by TLC). After the solution was cooled to room temperature, the solvent was removed at reduced pressure (rotovap) to afford a yellow solid. The latter was stirred in 20 mL of ethyl acetate for 30 min and then filtered to afford 210 mg (86%) of yellow crystals that gave one major spot on TLC. Recrystallization from dimethylformamide/1-butanol gave 101 mg (42%) of an analytical sample: mp 307–309 °C (sealed capillary); $[\alpha]^{25}_{589}$ −60.3° (*c* 0.83); IR (KBr) ν 3350, 2980, 2930, 2880, 1670, 1640, 1550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (3 H, t, *J* = 7.5 Hz), 1.39 (3 H, d, *J* = 7 Hz), 1.91 (3 H, s), 2.08 (3 H, s), 2.30 (3 H, s), 2.5–2.7 (6 H, m), 4.8–5.1 (1 H, m), 6.10 (1 H, m), 7.0–7.5 (5 H, m), 10.13 (1 H, s), 11.00 (1 H, s); ^1H NMR (DMSO-d_6) δ 1.04 (3 H, t, *J* = 7 Hz), 1.26 (3 H, d, *J* = 7 Hz), 1.72 (3 H, s), 1.96 (3 H, s), 2.07 (3 H, s), 2.15–2.35 (6 H, m), 4.84 (1 H, q, *J* = 7 Hz), 5.89 (1 H, s), 7.0–7.4 (5 H, m), 9.70 (1 H, s), 10.22 (1 H, s); UV ϵ^{405}_{max} = 33 800 ($CHCl_3$), ϵ^{414}_{max} = 32 200 (DMSO); CD $\Delta\epsilon^{402}_{max}$ = −3.1, $\Delta\epsilon^{446}$ = 0, $\Delta\epsilon^{446}_{max}$ = +1.3 (4.4 × 10^{-5} M in $CHCl_3$), $\Delta\epsilon^{413}_{max}$ = −1.3 (3.8 × 10^{-5} M in DMSO). Anal. Calcd for $C_{15}H_{31}N_3O_2$ (405.52): C, 74.04; H, 7.71; N, 10.36. Found: C, 73.84; H, 7.88; N, 10.26.

(+)-Xanthobilirubic Acid (*S*)-α-Methylbenzylamide (2). This enantiomer was prepared as above, in 88% yield (61% recrystallized), with (*S*)-(−)-α-methylbenzylamine. It had the same melting point and spectral data as above, except $[\alpha]^{25}_{589}$ +60.7° (*c* 0.36) and CD $\Delta\epsilon^{402}_{max}$ = +3.1, $\Delta\epsilon^{432}$ = 0, $\Delta\epsilon^{446}_{max}$ = −1.3 (4.4 × 10^{-5} M in $CHCl_3$), $\Delta\epsilon^{413}_{max}$ = +1.3 (3.6 × 10^{-5} M in DMSO).

(±)-Xanthobilirubic Acid (*R,S*)-α-Methylbenzylamide (5). The racemic mixture was prepared as above, in 82% yield, with racemic α-methylbenzylamine. It had mp 298–299 °C (sealed capillary) and the same spectral properties as above except $[\alpha]_{589}$ 0° and $\Delta\epsilon$ = 0 (in $CHCl_3$ or DMSO from 320–520 nm).

(−)-Xanthobilirubic Acid (*R*)-1-(1-Naphthyl)ethylamide (3). This amide was prepared in 85% yield (55% recrystallized) as above with (*R*)-(+)-1-(1-naphthyl)ethylamine: mp 308–309 °C (sealed capillary); $[\alpha]^{25}_{589}$ −109.2° (*c* 0.36); IR (KBr) ν 3350, 3970, 2920, 2870, 1665, 1635, 1540 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (3 H, t, *J* = 7 Hz), 1.56 (3 H, d, *J* = 8 Hz), 1.88 (3 H, s), 2.06 (3 H, s), 2.24 (3 H, s), 2.25–2.75 (6 H, m), 5.5–5.8 (1 H, m), 6.06 (1 H, s), 7.0–7.5 (7 H, m), 10.01 (1 H, s), 10.87 (1 H, s); ^1H NMR (DMSO-d_6) δ 1.08 (3 H, t, *J* = 7 Hz), 1.43 (3 H, t, *J* = 7 Hz), 1.77 (3 H, s), 1.99 (3 H, s), 2.09 (3 H, s), 2.1–2.4 (6 H, m), 4.65 (1 H, q, *J* = 7 Hz), 5.92 (1 H, s), 7.3–8.1 (7 H, m), 9.74 (1 H, s), 10.24 (1 H, s); UV ϵ^{405}_{max} = 32 300 ($CHCl_3$), ϵ^{413}_{max} = 31 900 (DMSO); CD $\Delta\epsilon^{404}_{max}$ = −5.2, $\Delta\epsilon^{432}$ = 0, $\Delta\epsilon^{447}_{max}$ = +2.0 (5.0 × 10^{-5} M in $CHCl_3$), $\Delta\epsilon^{413}_{max}$ = −1.7 (3.8 × 10^{-5} M in DMSO). Anal. Calcd for $C_{29}H_{33}N_3O_2$ (455.57): C, 76.45; H, 7.30; N, 9.22. Found: C, 76.15; H, 7.50; N, 9.20.

(+)-Xanthobilirubic Acid (*R*)-1-(1-Naphthyl)ethylamide (4). This enantiomeric amide was prepared as above in 80% yield (51% recrystallized) with *S*-(−)-1-(1-naphthyl)ethylamine. It had the same melting point and spectral data as above, except $[\alpha]^{25}_{589}$ +101.2° (*c* 0.33) and CD $\Delta\epsilon^{403}_{max}$ = +5.2, $\Delta\epsilon^{432}$ = 0, $\Delta\epsilon^{447}_{max}$ = −2.0 (4.9 × 10^{-5} M in $CHCl_3$); $\Delta\epsilon^{412}_{max}$ = +1.7 (4.1 × 10^{-5} M in DMSO).

(±)-Xanthobilirubic Acid (*R,S*)-1-(1-Naphthyl)ethylamide (6). The racemic amide was prepared as above in 86% yield from racemic 1-(1-naphthyl)ethylamine. It had mp 289–290 °C (sealed capillary) and the same spectral properties as above, except $[\alpha]_{589}$ 0° and $\Delta\epsilon$ (in $CHCl_3$ or DMSO from 320–520 nm).

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Photochemical Heterocyclization of Functionalized Dienamines

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A series of functionalized dienamines were prepared by base-catalyzed isomerization of *N*-vinylaziridines. Photochemical cyclization of these N-unsubstituted dienamines yielded predominantly pyrroline or pyrrole derivatives.

Photochemical reactions of aryl vinyl heteroatom systems have been studied extensively[1-9] and are often a convenient route to condensed heterocyclic compounds.[10,11] In most of the heterosystems that have been investigated,

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