Reductions of the tosylate with Super Hydride in THF or with $LiAlH_4/AlCl_3$ at room temperature resulted only in the reduction of the ester moiety: ^1H NMR δ 1.3-1.9 (m, 10 H), 2.06 (br s, 1 H), 2.45 (br s, 1 H), 2.46 (s, 3 H), 2.92 (br s, 1 H), 3.58 (s, 2 H), 4.11 (d, J = 7 Hz, 2 H), 5.34 (t, J = 7 Hz, 1 H), 7.32 (d, J = 8 Hz, 2 H), 7.76 (d, J = 8 Hz, 2 H).

(*aS*)-(5-Methyl-2-adamantylidene)acetaldehyde (25). Alcohol **24** was oxidized with MnO_2 in dichloromethane in the usual manner; the yield of aldehyde **25** was 97%. An analytical sample was purified by radial chromatography (hexane-5% diethyl ether): $[\alpha]^{25}_{546}$ -4.4° (c 1, cyclohexane); IR (film) 2910, 2850, 1675, 1630, 1460, 1210, 1140, 950 cm^{-1}; ^1H NMR δ 0.84 (s, 3 H), 1.50-1.95 (m, 10 H), 2.10 (br s, 1 H), 2.57 (br s, 1 H), 3.64 (br s, 1 H), 5.82 (d, J = 8 Hz, 1 H), 10.02 (d, J = 8 Hz, 1 H); UV ϵ 66 (345 nm), 20600 (236.5 nm); CD $\Delta\epsilon$ +0.13 (345 nm), -1.9 (235 nm). Anal. Calcd for $C_{13}H_{18}O$: C, 82.05; H, 9.53. Found: C, 82.05; H, 9.44.

(*aS*)-(5-Methyl-2-adamantylidene)propene (26). This compound was prepared from aldehyde **25** according to the procedure for preparation of **19** (diethyl ether was used as solvent instead of THF). The yield, after purification by radial chromatography (hexane), was 57%: $[\alpha]^{25}_{546}$ -3.5° (c 1, cyclohexane); IR (film) 3070 (w), 3030 (w), 2900, 2840, 1650, 1600 (w), 1460, 990, 900 cm^{-1}; ^1H NMR δ 0.78 (s, 3 H), 1.4-1.8 (m, 10 H), 2.02 (br s, 1 H), 2.41 (br s, 1 H), 3.05 (br s, 1 H), 4.94 (dd, J = 11, 2 Hz, 1 H), 5.10 (dd, J = 16.5, 2 Hz, 1 H), 5.77 (d, J = 11 Hz, 1 H), 6.62 (sextet, J = 16.5, 11, 11 Hz, 1 H); UV ϵ 30600 (240 nm); CD $\Delta\epsilon$ -0.45 (236 nm). Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.13; H, 10.67.

(*aS*)-(5-Methyl-2-adamantylidene)acetone (27). Aldehyde **25** (0.38 g, 2 mmol) in dry diethyl ether (5 mL) was treated at 0 °C with 3 mL of 1.6 M MeLi. After 1 h the reaction was quenched with water, and the products were extracted with diethyl ether. The crude mixture of methylcarbinols (0.39 g) was dissolved in hexane (35 mL) and oxidized with MnO_2 (3.5 g) for 2 h. The solution was filtered and evaporated. The residual oil was purified by radial chromatography (hexane-5% diethyl ether). The yield of **27** was 0.33 g (81%): $[\alpha]^{25}_{546}$ -10.9° (c 1.4, cyclohexane); IR (film) 2900, 2840, 1690, 1460, 1360, 1180, 950 cm^{-1}; ^1H NMR δ 0.80 (s, 3 H), 1.5-1.9 (m, 10 H), 2.03 (br s, 1 H), 2.18 (s, 3 H), 2.37 (br s, 1 H), 4.06 (br s, 1 H), 5.97 (s, 1 H); UV ϵ 79 (327 nm), 15400 (240 nm); CD $\Delta\epsilon$ -0.031 (332 nm), -0.8 (240 nm). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.35; H, 9.94.

Methyl (*aS*)-(5-Methyl-2-adamantylidene)acetate (28).[16] Aldehyde **25** (228 mg, 1.2 mmol) was dissolved in *tert*-butyl alcohol (25 mL) and 2-methyl-2-butene (6 mL). A solution of sodium dihydrogen phosphate (1.0 g, 8.3 mmol) and 80% sodium chlorite (1.25 g, 11 mmol) in water (10 mL) was added dropwise over a 10-min period. The reaction mixture was stirred overnight at room temperature. After removal of volatiles in vacuo the residue was dissolved in water (30 mL) and extracted with hexane. The aqueous layer was acidified (pH 3) with 2 N HCl and extracted with diethyl ether. The ethanol solution was washed with water, dried, and treated with ethereal diazomethane. The ester **28** was purified by radial chromatography (hexane-1% diethyl ether): yield 175 mg (67%); $[\alpha]^{25}_{546}$ -14.4° (c 1, cyclohexane); IR (film) 2900, 2840, 1720, 1650, 1460, 1440, 1395, 1245, 1230, 1170, 1040, 875 cm^{-1}; ^1H NMR δ 0.82 (s, 3 H), 1.45-1.90 (m, 10 H), 2.04 (br s, 1 H), 2.46 (br s, 1 H), 3.70 (s, 3 H), 4.07 (br s, 1 H), 5.59 (s, 1 H); UV ϵ 17200 (224 nm); CD $\Delta\epsilon$ -0.27 (253 nm), -0.5 (227 nm). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.20; H, 9.05.

Acknowledgment. This work was supported by a grant from the National Science Foundation, for which we are grateful. We thank Prof. D. A. Lightner and Prof. G. Snatzke for the low-temperature CD measurements. The Allinger MMP2 calculations were conducted with the assistance of Dr. J. Koput. We also thank Prof. Allinger for making his facilities available to us. Partial support to J.K.G. by the RP.II.13.2.10 program is gratefully acknowledged.

Exciton Effects in Chiral Planar 1,3-Dienes and α,β-Unsaturated Carbonyl Compounds. Configurational Application

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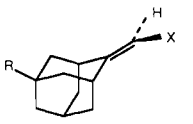
Abstract: A new application of exciton coupling between a benzoate chromophore and planar 1,3-diene as well as α,β-unsaturated carbonyl chromophore (aldehyde, ketone, or ester) for determination of the absolute configuration of axially dissymmetric molecules is reported. The effect of Z/E configuration of the chromophore on exciton interaction is noted.

Exciton coupling in circular dichroic spectroscopy,[1] which depends on Davydov splitting of excitations in two-chromophoric systems,[2] is based on the pioneering work of Kuhn[3] and Kirkwood.[4] It has found numerous applications in structural organic chemistry due largely to the extensive work of Nakanishi and Harada.[5] The scope of applications covers vicinal and distant dibenzoate and tribenzoate systems, biaromatic and heteroaromatic systems, and systems having two different chromophores whose π-π^* transition excitations are close in energy. CD exciton chirality has been used, with confidence, to establish absolute configurations of molecules and rivals the Bijvoet X-ray method as a nonempirical means of doing so.[5]

We have found this method extremely useful for determining absolute configuration of compounds possessing so-called "axial dissymmetry" (Charts I and II, R = OCOPh, X = CH=CH_2, CHO, COOMe, COMe), where the two chromophores, the benzoate chromophore and a conjugated diene or conjugated

Chart I



(aS)-(-)-1, R=OH, X=COOMe
(aS)-(-)-2, R=OCOPh, X=COOMe
(aS)-(+) 3, R=OH, X=CHO
(aS)- 4, R=OH, X=CH_2OH
(aS)-(-)- 5, R=OCOPh, X=CH_2OCOPh
(aS)- 6, R=OCOPh, X=CH_2OH
(aS)-(-)- 7, R=OCOPh, X=CHO
(aS)-(-)-8, R=OH, X=CH=CH_2
(aS)-(-)-9, R=OCOPh, X=CH=CH_2
(aS)-(+)-10, R=OH, X=COMe
(aS)-(-)- 11, R=OCOPh, X=COMe
(aS)-(-)- 12, R=CH_2OH, X=COOMe
(aS)-(-)- 13, R=CH_2OCOPh, X=COOMe

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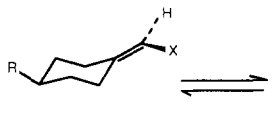
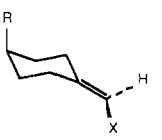
Chart II



(aS)-(-)-**14**, R=OH, X=COOMe
(aS)-(-)-**15**, R=OCOPh, X=COOMe
(aS)-(-)-**16**, R=OH, X=CHO
(aS)-(-)-**17**, R=OCOPh, X=CHO
(aS)-(+)-**18**, R=OH, X=CH=CH$_2$
(aS)-(-)-**19**, R=OCOPh, X=CH=CH$_2$



(aS)-(-)-**20**, R=OH, X=COMe
(aS)-(-)-**21**, R=OCOPh, X=COMe
(aS)-**22**, R=OH, X=CH$_2$OH
(aS)-**23**, R=OCOPh, X=CH$_2$OCOPh
(aS)-**24**, R=OCOPh, X=CH$_2$OH

(aS)-(+)-**25**, R=OH, X=COOMe
(aS)-(-)-**26**, R=OCOPh, X=COOMe

carbonyl chromophore, are placed in the 1,4-positions of the cyclohexane ring (or in equivalent 2,5-positions in the adamantane ring; vide infra). Such an arrangement of the chromophores remains noncoplanar, despite the possible conformational changes, and thus allows the application of the exciton chirality method.

We have also examined the exciton effects in the CD spectra of the isomeric 4-benzoates in the 2-adamantylidene series. Although the absolute configurations of the parent 4-hydroxy-2-adamantanones are known,[6] we required a method for establishing relative Z/E configurations, pair wise, for the alcohols **27**/**31**, **29**/**33**, **35**/**39**, and **37**/**41**. The exciton effects of the corresponding benzoates allowed us to assign the relative configuration of the isomeric alcohols. The isomeric compounds were prepared from the mixture of isomeric hydroxy esters **27**/**31** and **35**/**39**, which were in turn obtained by an Horner–Emmons olefination of the corresponding (1*R*)-4(a)- and (1*R*)-4(e)-hydroxy-2-adamantanones.

Preparative Work

Although syntheses of benzoates from alcohols is considered a trivial problem, we observed some difficulties in their preparation when an α,β-unsaturated aldehyde group was present in the molecule. We have found that the preferred method for benzoylation involved the use of 4-(dimethylamino)pyridine, a hypernucleophilic acylation agent, which allowed us to carry out the reaction at room temperature even with a tertiary hydroxy group in the 5-position of the adamantane ring. This method enabled us to avoid side reactions as well as racemization in all the cases we have studied, except for the preparation of aldehyde benzoates **7** and **17**. Direct benzoylation of hydroxy aldehyde **3** at room temperature gave only traces of racemic benzoate **7**, and benzoylation of **16** at −50 °C yielded only racemic benzoate **7**. In order to circumvent this problem benzoates **7** and **17** were prepared indirectly from diols **4** and **22**, which readily yielded chiral dibenzoates **5** and **23**. Selective hydrolysis of the primary allylic benzoate group afforded monobenzoates **6** and **24**, which were then oxidized with MnO_2 to the desired aldehyde benzoates **7** and **17**.

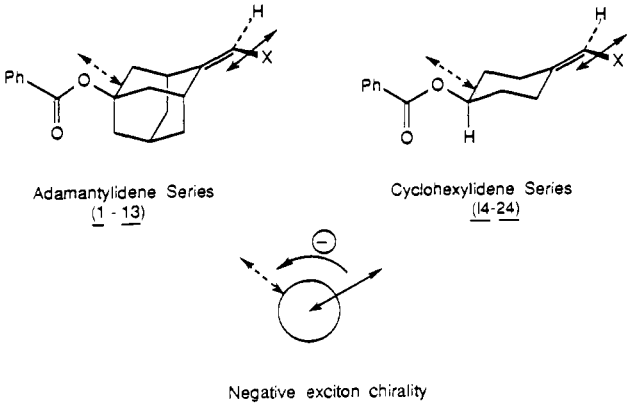
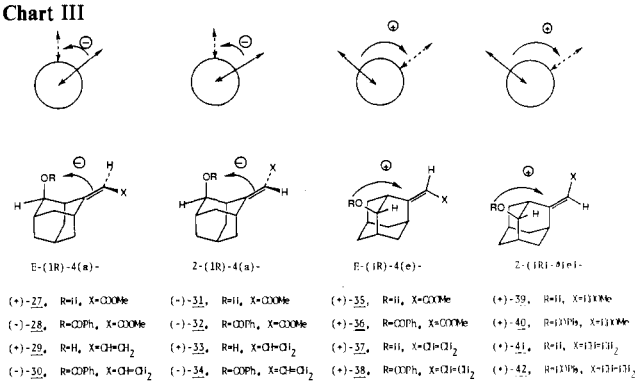


Figure 1.

Chart III



E-(1R)-4(a)- Z-(1R)-4(a)- E-(1R)-4(e)- Z-(1R)-4(e)-

(+)-**27**, R=H, X=COOMe (-)-**31**, R=H, X=COOMe (+)-**35**, R=H, X=COOMe (+)-**39**, R=H, X=COOMe
(-)-**28**, R=COPh, X=COOMe (-)-**32**, R=COPh, X=COOMe (+)-**36**, R=COPh, X=COOMe (+)-**40**, R=COPh, X=COOMe
(+)-**29**, R=H, X=CH=CH$_2$ (+)-**33**, R=H, X=CH=CH$_2$ (+)-**37**, R=H, X=CH=CH$_2$ (+)-**41**, R=H, X=CH=CH$_2$
(-)-**30**, R=COPh, X=CH=CH$_2$ (-)-**34**, R=COPh, X=CH=CH$_2$ (+)-**38**, R=COPh, X=CH=CH$_2$ (+)-**42**, R=COPh, X=CH=CH$_2$

Discussion

The analysis of the exciton Cotton effects is based on the following premises.[5]

(a) The conformation of the benzoate group is s-trans, as shown in Figure 1. For the secondary alcohol benzoates the average conformation is that in which the carbonyl group is synperiplanar with the carbinol C–H bond.

(b) The dipole moment for the charge-transfer transition of the benzoate chromophore is directed along the longitudinal axis of the chromophore (Figure 1). Thus to a first approximation the dipole moment is parallel to the carbinol C–O bond in secondary alcohol benzoates (see Chart III). No preferred orientation is expected for the benzoate of tertiary alcohol in the adamantane series and the effective direction of the dipole moment is assumed to be along the carbinol C–O bond.

(c) The direction of the dipole moment for the electrically allowed transition of the C=CHX group has not been rigorously determined, but in conjugated systems it is assumed to fall into the long axis of the chromophore. For the sake of simplicity, in the qualitative analysis of the exciton Cotton effects we place the dipole moment in the center of the C–X bond, its direction being parallel to the axis of the C=C bond[7] (Figure 1 and Chart III).

(d) In order to determine the sign of the exciton chirality one establishes whether the electric transition moments of the two chromophores constitute a right-handed or left-handed screwness; i.e., a positive exciton chirality is when the acute angle made by going from the nearest chromophore (solid double arrow) to the farthest one (dashed double arrow) is in a clockwise direction and a negative chirality when the direction is counterclockwise.

negative chirality positive chirality

(1) Harada, N.; Nakanishi, K. *Acc. Chem. Res.* **1972**, *5*, 257.
(2) (a) Davydov, A. S. *Theory of Molecular Excitons* (translation by M. Kasha and M. Oppenheimer, Jr.); McGraw-Hill: New York, 1962. (b) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371. (c) Kasha, M. In *Spectroscopy of the Excited State*; DiBartolo, B., Ed.; Plenum: New York, 1976.
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Table I. Chiroptical Data for the Isomeric 5-Benzoates of the 2-Adamantylidene and 4-Cyclohexylidene Series[a]

compd	CD Δε (nm) n–π*	CD Δε (nm) exciton	UV ε (λ, nm)
(*aS*)-(−)-**2**	2.0 sh (248)	−10.5 (232); +8.1 (217)	31 600 (225)
(*aS*)-(−)-**7**	+0.59 (347)	−15.6 (237); +3.0 (221)	65 (346), 35 000 (232)
(*aS*)-(−)-**9**		−5.1 (237); +2.7 (208)	44 000 (237)
(*aS*)-(−)-**11**	−0.26 (335)	−12.9 (239); +9.1 (223)	67 (331), 27 700 (230)
(*aS*)-(−)-**13**	−0.9 sh (249)	−6.2 (232); +1.7 (216)	30 800 (225)
(*aS*)-(−)-**15**	−0.5 sh (255)	−15.5 (229); +5.9 (217)	26 400 (224)
(*aS*)-(−)-**17**	+0.27 (348)	−24.4 (236); +13.1 (221)	53 (347), 34 200 (230)
(*aS*)-(−)-**19**		−11.8 (238); +5.4 (221)	41 800 (236)
(*aS*)-(−)-**21**	−0.1 (335)	−22.8 (238); +14.8 (222)	54 (329), 27 000 (231)
(*aS*)-(−)-**26**		−9.2 (237); +16.9 (210)	21 000 (228)

[a] In cyclohexane, corrected to 100% ee.

All the benzoates (shown in Charts I and II) prepared for the present study show negative exciton Cotton effects at their long-wavelength UV maximum (Table I). This coupling predicts that the absolute configurations are as shown in Figure 1. The consistent observation of a negative exciton coupled CD spectra is not surprising, as all the precursor alcohols in each series have been prepared from the same chiral starting materials,[8] the hydroxy esters **1** and **14**, which in turn have had their configurations related.[9] It is evident that exciton coupling gives Cotton effects of the same sign, regardless of the nature of the substituent X. However, certain variations in the amplitude of the observed exciton Cotton effects require discussion.

Compounds with the rigid adamantane skeleton, **2**, **7**, and **11**, show amplitudes of ca. −20, the exception being diene benzoate **9**, $A = -7.8$. The amplitude of the exciton Cotton effect of benzoate **13** is much lower as compared to **2**. This may be the result of a larger distance between the benzoate and the α,β-unsaturated ester chromophore due to the additional methylene group in **13**.

The amplitudes of the conformationally mobile benzoates **15**, **17**, **19**, and **21** are high compared to their rigid adamantylidene analogues. This apparently reflects the contribution of the axial (a) conformer in the equilibrium (Chart II), which carries the same negative chirality as the equatorial (e) conformer but has the two interacting chromophores at a shorter distance. The high amplitude of benzoate **21** may also reflect the tendency of the α,β-unsaturated ketone to exist largely in a cisoid conformation.[8]

Benzoate **26**, in which the four methyl groups in the 2,2,6,6-positions exert their steric interactions and force the α,β-unsaturated ester chromophore out of planarity,[9] still shows the effect of exciton coupling as well as reflecting the negative chirality of the bichromophoric system.

The assignment of absolute configuration to hydroxy esters **1**, **14**, and **25** by the exciton chirality method is further corroborated on the basis of their Cotton effects.[9]

Turning now to the series of 4-benzoates of the 2-adamantylidene skeleton (Chart III), we note that axial benzoates **28**, **30**, **32**, and **34** show strong negative exciton Cotton effects (Table II), in accordance with the chirality of the chromophoric system, based on the known absolute configuration.[6] It is evident, however, that in comparing the configurational isomers **28**/**32** and **30**/**34**, the latter of each pair, i.e., **32** and **34**, show exciton Cotton effects of at least twice the amplitude of that displayed by **28** and **30**. Thus conjugated ester benzoate **32** and diene benzoate **34** must have the two interacting chromophores at a closer distance; i.e., they have the *Z* conformation.

Equatorial benzoates **36**, **38**, **40**, and **42** display positive exciton Cotton effects (Table II), reflecting their positive chirality (Chart III). The differences between amplitudes of the exciton Cotton effects of the pairs of geometrical isomers **36**/**40** and **38**/**42**, although smaller than in the case of axial benzoates, allow assignment of the *Z* configuration to the latter compound of each pair, i.e., **40** and **42**. This conclusion is consistent with the configurations that have been established by NMR spectroscopy for these isomers.

Table II. Chiroptical Data for the Isomeric 4-Benzoates of the 2-Adamantylidene Series[a]

compd	CD Δε (nm)	UV ε (λ, nm)
(*E*)-(1*R*)-4(a)-(−)-**28**	−11.0 (230); +1.6 (215)	26 500 (223)
(*E*)-(1*R*)-4(a)-(−)-**30**	−25.1 (238); +10.6 (220)	31 200 (228)
(*Z*)-(1*R*)-4(a)-(−)-**32**	−43.5 (231); +11.3 (216)	26 400 (224)
(*Z*)-(1*R*)-4(a)-(−)-**34**	−51.6 (237); +18.7 (219)	35 700 (230)
(*E*)-(1*R*)-4(e)-(+)-**36**	+22.3 (232); −5.8 (215)	28 300 (229)
(*E*)-(1*R*)-4(e)-(+)-**38**	+18.7 (238); −11.9 (220)	29 400 (232)
(*Z*)-(1*R*)-4(e)-(+)-**40**	+24.0 (232); −15.3 (217)	27 500 (227)
(*Z*)-(1*R*)-4(e)-(+)-**42**	+26.0 (238); −17.9 (221)	35 800 (232)

[a] In cyclohexane, corrected to 100% ee.

Another regularity is observed in comparing the position of the UV maximum of each of the pairs of 4(a)/4(e) benzoates, i.e., **28**/**36**, **30**/**38**, **32**/**40**, and **34**/**42**. As the dihedral angle between the two chromophores becomes larger in the 4(e) derivatives, the UV maximum is red-shifted by 4–6 nm in the *E* isomers and 2–3 nm in the *Z* isomers. This pattern follows the angular dependence of UV maxima previously established for the di(*p*-substituted/benzoate) systems[10] and helps to assign the relative (axial or equatorial) configuration of the benzoate substituent.

In summary, it has been demonstrated that the exciton chirality method can be used effectively for the determination of absolute and relative configurations of axially dissymemetric derivatives of cyclohexane and adamantane.

Experimental Section

For general experimental procedures see ref 8.

The preparation of the alcohol precursors to the benzoates has been reported elsewhere.[8,9,11]

Methyl (*aS*)-(−)-(5-(Benzoyloxy)adamantylidene)acetate (2). Hydroxy ester **1** (80% ee,[8] 55 mg, 0.25 mmol) was dissolved in pyridine (0.4 mL) and heated with benzoyl chloride (0.06 mL, 0.5 mmol) at 100 °C for 4 h. After cooling, it was extracted with ether and 2 N HCl, and the extracts were washed with $NaHCO_3$ solution and evaporated. The product was purified by radical chromatography on silica gel using hexane–dichloromethane (1:1) as eluent: yield 78 mg (96%); $[\alpha]^{23}_{546}$ −47.8° (*c* 1.5, $CHCl_3$); ^1H NMR δ 1.7–2.6 (m, 11 H), 2.70 (br s, 1 H), 3.72 (s, 3 H), 4.31 (br s, 1 H), 5.65 (s, 1 H), 7.35–7.60 (m, 3 H), 7.65–8.05 (m, 2 H). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.62; H, 6.75. Found: C, 73.55; H, 6.86.

(*aS*)-(−)-(5-Hydroxyadamantylidene)ethanol Dibenzoate (5). Diol[8] **4** (195 mg, 1 mmol) in 1 mL of dichloromethane was added to a mixture of 4-(dimethylamino)pyridine (490 mg, 4 mmol) and benzoyl chloride (0.25 mL, 2 mmol) in 2 mL of dichloromethane. The solution was stirred for 3 h at room temperature, followed by filtration through silica gel with dichloromethane as solvent. The product (405 mg, quantitative yield) was further purified by radial chromatography using hexane–dichloromethane (1:1) as eluent: $[\alpha]^{25}_{546}$ −4.0° (*c* 1, cyclohexane); ^1H NMR δ 1.65–2.0 (m, 4 H), 2.15–2.50 (m, 7 H), 2.70 (br s, 1 H), 3.25 (br s, 1 H), 4.85 (d, J = 7.5 Hz, 2 H), 5.46 (t, J = 7.5 Hz, 1 H), 7.35–7.60 (m, 6 H), 7.90–8.10 (m, 4 H); UV (c 6.10 × 10^{-5}) λ_{228} ε 28 300.

(*aS*)-(−)-(5-(Benzoyloxy)adamantylidene)acetaldehyde (7). A mixture of dibenzoate **5** (250 mg, 0.62 mmol), 3 mL of MeOH, and 0.4 mL of 2 N NaOH was stirred at room temperature for 1 h. Methanol was evaporated in vacuo, and the residue was taken up in dichloromethane, dried over $MgSO_4$, and evaporated to give crude monobenzoate (209 mg; it contains some methyl benzoate). This was dissolved in dichloromethane (10 mL) and oxidized under nitrogen with 0.7 g of MnO_2 for 1.5 h. The mixture was filtered and the crude product (170 mg) was purified by radial chromatography with hexane–diethyl ether (4:1). The product (120 mg, 54%) had the following properties: mp 96–98 °C; $[\alpha]^{25}_{546}$ −16.6° (*c* 1.2, cyclohexane), ^1H NMR δ 1.8–2.1 (m, 4 H), 2.3–2.6 (m, 7 H), 2.80 (br s, 1 H), 3.87 (br s, 1 H), 5.86 (d, J = 10 Hz,

(7) This suggestion was made by Prof. James Brewster, Purdue University.
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(11) Walborsky, H. M.; Reddy, S. M., to be published.

1 H), 7.35–7.60 (m, 3 H), 7.98 (d, J = 8 Hz, 2 H), 10.40 (d, J = 10 Hz, 1 H). Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 77.07; H, 6.88.

(*aS*)-(−)-(5-(Benzoyloxy)adamantylidene)propene (9). This compound was prepared from **8** according to the procedure for preparation of **5**: 91% yield after radial chromatography purification (hexane–2% diethyl ether); $[\alpha]^{25}_{546}$ −17.0° (*c* 0.9, cyclohexane); ^{1}H NMR δ 1.65–1.95 (m, 4 H), 2.15–2.50 (m, 7 H), 2.65 (br s, 1 H), 3.27 (br s, 1 H), 5.01 (dd, J = 11, 2 Hz, 1 H), 5.15 (dd, J = 16.5, 2 Hz, 1 H), 5.82 (d, J = 11 Hz, 1 H), 6.60 (sextet, J = 16.5, 11, 11 Hz, 1 H), 7.35–7.55 (m, 3 H), 7.95–8.05 (m, 2 H). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.63; H, 7.48. Found: C, 81.56; H, 7.51.

(*aS*)-(−)-(5-(Benzoyloxy)adamantylidene)acetone (11). This compound was prepared[8] from **10** according to the procedure for preparation of **5**: 90% yield after radial chromatography (hexane–10% diethyl ether); $[\alpha]^{25}_{546}$ −34.5° (*c* 1.6, cyclohexane). Anal. Calcd for $C_{20}H_{22}O_2$: C, 77.42; H, 7.01. Found: C, 77.43; H, 7.06.

Methyl (*aS*)-(−)-(5-((Benzoyloxy)methyl)adamantylidene)acetate (13). Hydroxy ester[8] **12** (90% ee, 118 mg, 0.5 mmol) in dichloromethane (2 mL) was stirred overnight at room temperature with benzoyl chloride (0.12 mL, 1 mmol) and pyridine (0.16 mL, 2 mmol). After extractive workup and radial chromatography (hexane–dichloromethane (3:1)) the product was obtained in 72% yield (123 mg): $[\alpha]^{25}_{546}$ −36.6° (*c* 1.4, cyclohexane); IR (film) 3050 (w), 2920, 2850, 1720, 1650, 1600 (w), 1500 (w), 1480–1220, 1165, 1120, 1030, 870, 715 cm^{-1}; ^{1}H NMR δ 1.7–2.0 (m, 10 H), 2.13 (br s, 1 H), 2.55 (br s, 1 H), 3.70 (s, 3 H), 3.96 (s, 2 H), 4.18 (br s, 1 H), 5.64 (s, 1 H), 7.4–7.6 (m, 3 H), 8.05 (d, J = 8 Hz, 2 H). Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 74.04; H, 7.16.

Methyl (*aS*)-(−)-(4-(Benzoyloxy)cyclohexylidene)acetate (15). This compound was prepared[8] from hydroxy ester **14** (63% ee) according to the procedure for preparation of **5**: 92% yield after radial chromatography (hexane–5% diethyl ether) purification; $[\alpha]^{25}_{546}$ −32.5° (*c* 1, cyclohexane); IR (film) 3050 (w), 2940, 2850, 1720, 1660, 1605 (w), 1500 (w), 1480–1070, 1030, 870, 715 cm^{-1}; ^{1}H NMR δ 1.80–2.14 (m, 4 H), 2.29 (m, 1 H), 2.52 (m, 1 H), 2.92 (m, 1 H), 3.16 (m, 1 H), 3.70 (s, 3 H), 5.26 (m, 1 H), 5.71 (s, 1 H), 7.44 (m, 2 H), 7.55 (m, 1 H), 8.05 (m, 2 H). Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 70.21; H, 6.77.

(*aS*)-(−)-(4-(Benzoyloxy)cyclohexylidene)acetaldehyde (17). Diol[8] **22** was converted to dibenzoate **23** in quantitative yield by the method used for preparation of dibenzoate **5** (reaction time 15 min): ^{1}H NMR δ 1.86 (m, 2 H), 2.00 (m, 2 H), 2.2–2.4 (m, 2 H), 2.46 (m, 1 H), 2.62 (m, 1 H), 4.86 (d, J = 7 Hz, 2 H), 5.24 (m, 1 H), 5.53 (t, J = 7 Hz, 1 H), 7.44 (m, 4 H), 7.56 (m, 2 H), 8.06 (m, 4 H).

Dibenzoate **23** was selectively saponified according to the procedure for preparation of monobenzoate **7** (reaction time 1 h at 0 °C) to give monobenzoate **24**: ^{1}H NMR δ 1.56 (br s, 1 H), 1.80 (m, 2 H), 1.97 (m, 2 H), 2.21 (m, 2 H), 2.42 (m, 1 H), 2.52 (m, 1 H), 4.17 (d, J = 7 Hz, 2 H), 5.20 (m, 1 H), 5.46 (t, J = 7 Hz, 1 H), 7.42 (m, 2 H), 7.54 (m, 1 H), 8.04 (m, 2 H).

Standard MnO_2 oxidation of monobenzoate **24** in CH_2Cl_2 afforded aldehyde **17** in 40% overall yield (purified by radial chromatography (hexane–25% diethyl ether)): $[\alpha]^{25}_{546}$ −29.6° (*c* 1.6, cyclohexane); IR (film) 3060, 2950, 2850, 1720, 1680, 1610 (w), 1500 (w), 1460, 1285, 1125, 1035, 725 cm^{-1}; ^{1}H NMR δ 1.9–2.2 (m, 4 H), 2.40 (m, 1 H), 2.63 (m, 1 H), 2.83 (m, 1 H), 3.00 (m, 1 H), 5.32 (m, 1 H), 5.92 (d, J = 8 Hz, 1 H), 7.40–7.65 (m, 3 H), 8.05–8.15 (m, 1 H), 10.04 (d, J = 8 Hz, 1 H); MS (high resolution) calcd for $C_{15}H_{16}O_3$ 244.1099, found 244.1093.

(*aS*)-(−)-(4-(Benzoyloxy)cyclohexylidene)propene (19). This compound was prepared[8] from **18** according to the procedure for preparation of **5** (99% yield after radial chromatography purification (hexane–2% diethyl ether)): $[\alpha]^{25}_{546}$ −21.1° (*c* 1.1, cyclohexane); IR (film) 3070 (w), 3030 (w), 2940, 2850, 1720, 1650 (w), 1600 (w), 1495 (w), 1480–1200, 1120, 910, 820 cm^{-1}; ^{1}H NMR δ 1.70–1.90 (m, 2 H), 1.90–2.10 (m, 2 H), 2.15–2.40 (m, 2 H), 2.40–2.55 (m, 1 H), 2.55–2.70 (m, 1 H), 5.13 (dd, J = 11, 2 Hz, 1 H), 5.15 (dd, J = 17.2 Hz, 1 H), 5.23 (m, 1 H), 5.90 (d, J = 11 Hz, 1 H), 6.61 (sextet, J = 17, 11, 11 Hz, 1 H), 7.43 (t, J = 8 Hz, 2 H), 7.55 (t, J = 8 Hz, 1 H), 8.05 (d, J = 8 Hz, 2 H); MS (high reolsution) calcd for $C_{16}H_{18}O_2$ 242.1307, found 242.1309.

(*aS*)-(−)-(4-(Benzoyloxy)cyclohexylidene)acetone (21). This compound was prepared[8] from **20** according to the procedure for preparation of **5** (reaction time was shortened to 1 h and the temperature was lowered to −20 °C): 93% yield after radial chromatography purification (hexane–5% diethyl ether); $[\alpha]^{25}_{546}$ −40.4° (*c* 1.3, cyclohexane); IR (film) 3050 (w), 3020 (w), 2940, 2850, 1720, 1690, 1625, 1600 (w), 1495 (w), 1460, 1280, 1180, 1120, 1035, 915, 720 cm^{-1}; ^{1}H NMR δ 1.75–2.15 (m, 4 H), 2.21 (s, 3 H), 2.26 (m, 1 H), 2.48 (m, 1 H), 2.88 (m, 1 H), 3.13 (m, 1 H), 5.26 (m, 1 H), 6.09 (s, 1 H), 7.44 (m, 2 H), 7.56 (m, 1 H), 8.05 (m, 2 H). Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.51; H, 6.95.

Methyl (*aS*)-(−)-(4-(Benzoyloxy)-2,2,6,6-tetramethylcyclohexylidene)acetate (26). A mixture of methyl (*aS*)-(+)-(4-hydroxy-2,2,6,6-tetramethylcyclohexylidene)acetate[9] **(25)** (226 mg, $[\alpha]^{25}_{D}$ +31.31 ± 0.20°, 37.52% ee), 4-(dimethylamino)pyridine (366 mg, 3 equiv), and benzoyl chloride (210 mg, 1.50 equiv) in 5 mL of CH_2Cl_2 was stirred under a N_2 atmosphere for 30 min. The product was filtered through silica gel (5 g) using CH_2Cl_2 and concentrated. On radial chromatography using hexane–ether (100:5) was obtained a colorless liquid in quantitative yield (0.33 g) of methyl (*aS*)-(−)-(4-(benzoyloxy)-2,2,6,6-tetramethylcyclohexylidene) acetate **(26)**: $[\alpha]^{25}_{Hg}$ −3.92 ± 0.36° (*c* 0.97, $CHCl_3$); IR (CCl_4) 3070 (w), 3050 (w), 2950 (m), 1722, 1625, 1600, 1580 (w), 1470, 1452, 1435, 1400–1370, 1320–910 cm^{-1}; ^{1}H NMR δ 1.26 (s, 3 H), 1.28 (s, 3 H), 1.35 (s, 3 H), 1.41 (s, 3 H), 1.60–1.90 (m, 2 H), 1.98–2.15 (m, 2 H), 3.72 (s, 3 H), 5.43 (m, 1 H), 5.88 (s, 1 H), 7.38–7.62 (m, 3 H), 8.02 (doublet of multiplet, 2 H); ^{13}C NMR 29.27 (CH_3), 30.37 (CH_3), 31.92 (CH_3), 32.26 (CH_3), 37.25 (C), 38.55 (C), 42.81 (CH_2), 44.95 (CH_2), 51.38 (OCH_3), 68.39 (CH), 115.47 (olefinic CH), 128.30 (2 CH), 129.46 (2 CH), 130.45 (C), 132.80 (CH), 164.77 (C=O), 165.97 (C), 169.49 (C=O) ppm; UV (*c* 6.51 × 10^{-5}, cyclohexane) λ_{281} ε 980, λ_{274} ε 980, λ_{267} ε 770, λ_{228} ε 21 000, λ_{194} ε 39 900; CD (*c* 6.51 × 10^{-4}, cyclohexane) $\Delta\epsilon_{237}$ −3.45, $\Delta\epsilon_{210}$ +6.35. Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.72; H, 7.88. Found: C, 72.73; H, 7.90.

Methyl (*Z*)-(1*R*)-(4(a)-(Benzoyloxy)-2-adamantylidene)acetate (32). Benzoylation of methyl (*Z*)-(1*R*)-(4(a)-hydroxy-2-adamantylidene)-acetate[11] **(31)** (0.07 g, $[\alpha]^{25}_{Hg}$ −47.21 ± 0.71°, 84% ee) gave pure methyl (*Z*)-(1*R*)-(4(a)-(benzoyloxy)-2-adamantylidene)acetate **(32)** as a colorless liquid (0.099 g, 96% yield): $[\alpha]^{25}_{Hg}$ −146.53 ± 0.37° (*c* 0.49, $CHCl_3$); IR (CCl_4) 3070 (w), 3060 (w), 2970 (w), 2910, 2845, 1720, 1655, 1600 (w), 1580 (w), 1450, 1435, 1390–1020, 980–860 cm^{-1}; ^{1}H NMR δ 1.80–2.20 (m, 8 H), 2.23 (br s, 2 H), 2.50 (br s, 1 H), 3.53 (s, 3 H), 4.33 (br s, 1 H), 5.33 (br s, 1 H), 5.79 (s, 1 H), 7.30–7.60 (m, 3 H), 7.97 (dd, J = 1.47, 8.30 Hz, 2 H); ^{13}C NMR, see ref 11; UV (*c* 5.33 × 10^{-5}, 5.33 × 10^{-4}, cyclohexane) λ_{280} ε 780, λ_{273} ε 970, λ_{266} ε 910, λ_{224} ε 26 380, λ_{196} ε49 500; CD (*c* 5.33 × 10^{-4}, 5.33 × 10^{-3}, cyclohexane) $\Delta\epsilon_{279}$ −0.53, $\Delta\epsilon_{272}$ −0.68, $\Delta\epsilon_{266}$ −0.54 $\Delta\epsilon_{231}$ −36.53, $\Delta\epsilon_{216}$ +9.55, $\Delta\epsilon_{197}$ +23.60. Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.62; H, 6.75. Found: C, 73.64; H, 6.34.

Methyl (*E*)-(1*R*)-(4(a)-(Benzoyloxy)-2-adamantylidene)acetate (28). Methyl (*E*)-(1*R*)-(4(a)-hydroxy-2-adamantylidene)acetate[11] **(27)** (0.06 g, $[\alpha]^{25}_{Hg}$ +26.13 ± 0.40°, 84% ee) was benzoylated following the preparation of **26** to obtain 0.088 g (99%) of methyl (*E*)-(1*R*)-(4(a)-(benzoyloxy)-2-adamantylidene)acetate **(28)** as a liquid: $[\alpha]^{25}_{Hg}$ −9.09 ± 0.12° (*c* 0.63, $CHCl_3$); IR (CCl_4) 3070 (w), 3045 (w), 2978 (w), 2910, 2850, 1717, 1650, 1600 (w), 1580 (w), 1455, 1440, 1400–1000, 980–870 cm^{-1}; ^{1}H NMR δ 1.80–2.20 (m, 8 H), 2.23 (br s, 2 H), 2.70 (br s, 1 H), 3.69 (s, 3 H), 4.12 (br s, 1 H), 5.30 (br s, 1 H), 5.61 (s, 1 H), 7.35–7.60 (m, 3 H), 7.99 (d, J = 7.31 Hz, 2 H); ^{13}C NMR, see ref 11; UV (*c* 4.38 × 10^{-5}, 4.38 × 10^{-4}, cyclohexane) λ_{280} ε 700, λ_{272} ε 930, λ_{264} ε 900, λ_{223} ε 26 500; CD (*c* 4.38 × 10^{-4}, 4.38 × 10^{-3}, cyclohexane) $\Delta\epsilon_{279}$ −0.29, $\Delta\epsilon_{272}$ −0.28, $\Delta\epsilon_{251}$ +0.51, $\Delta\epsilon_{230}$ −9.30, $\Delta\epsilon_{215}$ +1.36, $\Delta\epsilon_{205}$ −2.05, $\Delta\epsilon_{195}$ +15.39. Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.62; H, 6.75. Found: C, 73.76; H, 6.78.

Methyl (*E*)-(1*R*)-(4(e)-(Benzoyloxy)-2-adamantylidene)acetate (36) and Methyl (*Z*)-(1*R*)-(4(e)-(Benzoyloxy)-2-adamantylidene)acetate (40). To a stirred solution of an *E* and *Z* mixture of methyl (1*R*)-(4-(e)-hydroxy-2-adamantylidene)acetates[11] **35** and **39** (0.20 g) in 1 mL of CH_2Cl_2 under a N_2 atmosphere was added 4-(dimethylamino)pyridine (0.33 g, 3 equiv) and benzoyl chloride (0.19 g, 1.5 equiv). After 30 min the mixture of products was filtered through silica gel (5 g) using CH_2Cl_2 and concentrated. The mixture of two benzoates was carefully separated by radial chromatography using hexane–ether solvent mixtures. The less polar fraction gave methyl (*E*)-(1*R*)-(4(e)-(benzoyloxy)-2-adamantylidene)acetate **(36)** as a colorless liquid (0.12 g): $[\alpha]^{25}_{Hg}$ +74.32 ± 0.31° (*c* 0.41, $CHCl_3$); IR (CCl_4) 3070 (w), 3050 (w), 3015 (w), 2970 (w), 2920, 2850, 1720, 1650, 1600 (w), 1580 (w), 1470–1440, 1340–1230, 1200–1020, 990–870 cm^{-1}; ^{1}H NMR δ 1.60–2.50 (m, 10 H), 2.72 (br s, 1 H), 3.70 (s, 3 H), 4.10 (br s, 1 H), 5.11 (br s, 1 H), 5.72 (s, 1 H), 7.40–7.70 (m, 3 H), 8.05–8.20 (m, 2 H); ^{13}C NMR, see ref 11; UV (*c* 5.52 × 10^{-5}, cyclohexane) λ_{282} ε 724, λ_{274} ε 1086, λ_{268} ε 1123, λ_{229} ε 28 300, λ_{194} ε 43 400; CD (*c* 5.52 × 10^{-4}, cyclohexane) $\Delta\epsilon_{232}$ +18.74, $\Delta\epsilon_{215}$ −4.89, $\Delta\epsilon_{200}$ −4.07. Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.62; H, 6.75. Found: C, 73.70; H, 6.80.

The more polar fraction (0.11 g) solidified on standing to yield methyl (*Z*)-(1*R*)-(4(e)-(benzoyloxy)-2-adamantylidene)acetate **(40)**: mp 131–134 °C; $[\alpha]^{25}_{Hg}$ +50.86 ± 0.23° (*c* 0.62, $CHCl_3$); IR (CCl_4) 3070 (w), 3050 (w), 2980 (w), 2920, 2850, 1720, 1655, 1600 (w), 1470–1435, 1380–1230, 1170–870 cm^{-1}; ^{1}H NMR δ 1.50–2.48 (m, 11 H), 3.69 (s, 3 H), 4.33 (br s, 1 H), 5.10 (br s, 1 H), 5.71 (s, 1 H), 7.40–7.65 (m, 3 H), 8.05–8.20 (m, 2 H); ^{13}C NMR, see ref 11; UV (*c* 4.81 × 10^{-5}, cyclohexane) λ_{282} ε 831, λ_{274} ε 1081, λ_{268} ε 1164, λ_{227} ε 27 500, λ_{194} ε

42 600; CD (c 4.81 × 10^{-4}, cyclohexane) $\Delta\epsilon_{232}$ -20.24, $\Delta\epsilon_{217}$ -12.92, $\Delta\epsilon_{200}$ -9.03. Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.62; H, 6.75. Found: C, 73.65; H, 6.88.

(Z)-(1R)-(4(a)-(Benzoyloxy)-2-adamantylidene)propene (34). (Z)-(1R)-(4(a)-Hydroxy-2-adamantylidene)propene[11] (**33**) (20 mg, $[\alpha]^{25}_{Hg}$ +25.23 ± 0.31°, 84% ee) was benzoylated as earlier to give 29 mg of (Z)-(1R)-(4(a)-(benzoyloxy)-2-adamantylidene)propene (**34**) as a colorless liquid: $[\alpha]^{25}_{Hg}$ -168.69 ± 0.08° (c 0.57, $CHCl_3$); IR (CCl_4) 3070 (w), 3050 (w), 3030 (w), 2910, 2850, 1800 (w), 1717, 1655, 1600, 1580 (w), 1450, 1340, 1320, 1275, 1180, 1120, 1100-900 cm^{-1}; ^1H NMR δ 1.60-2.10 (m, 8 H), 2.20 (br d, 1 H), 2.22 (br s, 1 H), 2.44 (br s, 1 H), 3.31 (br s, 1 H), 4.88 (dd, J = 1.83, 10.37 Hz, 1 H), 5.09 (dd, J = 1.83, 16.78 Hz, 1 H), 5.26 (br s, 1 H), 5.98 (d, J = 10.98 Hz, 1 H), 6.52 (sextet, J = 10.38, 10.99, 16.48 Hz, 1 H), 7.33-7.59 (m, 3 H), 7.96 (dd, J = 1.83, 8.54 Hz, 2 H); ^{13}C NMR, see ref 11; UV (c 4.28 × 10^{-5}, 4.28 × 10^{-4}, cyclohexane) λ_{320} ε 150, λ_{304} ε 280, λ_{280} ε 1000, λ_{273} ε 1138, λ_{267} ε 1054, λ_{247} ε 17 600, λ_{238} ε 30 300, λ_{230} ε 35 700, λ_{195} ε 43 900; CD (c 4.28 × 10^{-4}, 4.28 × 10^{-3}, cyclohexane) $\Delta\epsilon_{318}$ -0.075, $\Delta\epsilon_{304}$ -0.11, $\Delta\epsilon_{279}$ -0.82, $\Delta\epsilon_{272}$ -1.03, $\Delta\epsilon_{265}$ -0.89, $\Delta\epsilon_{237}$ -43.40, $\Delta\epsilon_{219}$ +15.75, $\Delta\epsilon_{195}$ +38.50. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.63; H, 7.48. Found: C, 81.70; H, 7.50.

(E)-(1R)-(4(a)-(Benzoyloxy)-2-adamantylidene)propene (30). Following an earlier procedure,[11] 10 mg of (E)-(1R)-(4(a)-hydroxy-2-adamantylidene)propene (**29**) ($[\alpha]^{25}_{Hg}$ +16.76 ± 3.30°, 84% ee) was benzoylated to yield 14 mg of pure (E)-(1R)-(4(a)-(benzoyloxy)-2-adamantylidene)propene (**30**): $[\alpha]^{26}_{Hg}$ -78.03 ± 0.40° (c 0.27, $CHCl_3$); IR ($CHCl_3$) 2920, 2860, 1715, 1655, 1605 (w), 1590 (w), 1470-1460, 1350, 1325, 1285, 1185-910 cm^{-1}; ^1H NMR δ 1.70-2.30 (m, 10 H), 2.64 (br s, 1 H), 3.07 (br s, 1 H), 4.97 (m, J = 0.64, 2.07, 10.15 Hz, 1 H), 5.10 (m, J = 0.61, 2.07, 17.23 Hz, 1 H), 5.26 (br s, 1 H), 5.79 (d, J = 10.92 Hz, 1 H), 6.65 (sextet, J = 10.20, 10.63, 16.84 Hz, 1 H), 7.30-7.60 (m, 3 H), 8.00 (dd, J = 2.04, 7.51 Hz, 2 H); UV (c 3.97 × 10^{-5}, 3.97 × 10^{-4}, cyclohexane) λ_{279} ε 1200, λ_{272} ε 1300, λ_{265} ε 1186, λ_{248} ε 14 100, λ_{238} ε 25 400, λ_{228} ε 31 200, λ_{196} ε 48 800; CD (c 3.97 × 10^{-4}, 3.97 × 10^{-3}, cyclohexane) $\Delta\epsilon_{278}$ -0.62, $\Delta\epsilon_{271}$ -0.74, $\Delta\epsilon_{288}$ -21.11, $\Delta\epsilon_{220}$ +8.97. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.63; H, 7.48. Found: C, 82.00; H, 7.80.

(Z)-(1R)-(4(e)-(Benzoyloxy)-2-adamantylidene)propene (42). Benzoylation of (Z)-(1R)-(4(e)-hydroxy-2-adamantylidene)propene[11] (**41**) (10 mg, $[\alpha]^{26}_{Hg}$ +31.65 ± 1.07°, 84% ee) as described earlier gave after purification 13 mg of (Z)-(1R)-(4(e)-(benzoyloxy)-2-adamantylidene)-propene (**42**): $[\alpha]^{26}_{Hg}$ +74.94 ± 0.23° (c 0.44, $CHCl_3$); IR ($CHCl_3$) 2920, 2860, 1715, 1650, 1605, 1590, 1470, 1460, 1355, 1325, 1285, 1130, 1100-910 cm^{-1}; ^1H NMR δ 1.60-2.40 (m, 10 H), 2.42 (br s, 1 H), 3.28 (br s, 1 H), 5.00 (dd, J = 2.05, 10.10 Hz, 1 H), 5.08 (br s, 1 H), 5.16 (dd, J = 1.99, 16.65 Hz, 1 H), 5.90 (d, J = 10.98 Hz, 1 H), 6.62 (sextet, J = 10.45, 10.67, 16.86 Hz, 1 H), 7.40-7.65 (m, 3 H), 8.10 (dd, J = 1.51, 8.86 Hz, 2 H); UV (c 5.61 × 10^{-5}, 5.61 × 10^{-4}, cyclohexane) λ_{279} ε 780, λ_{271} ε 969, λ_{247} ε 19 700, λ_{237} ε 34 600, λ_{232} ε 35 800, λ_{196} ε 43 500; CD (c 5.61 × 10^{-4}, 5.61 × 10^{-3}, cyclohexane) $\Delta\epsilon_{279}$ +0.18, $\Delta\epsilon_{271}$ +0.38, $\Delta\epsilon_{238}$ +21.91, $\Delta\epsilon_{221}$ -15.10. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.63; H, 7.48. Found: C, 81.76; H, 7.19.

(E)-(1R)-(4(e)-(Benzoyloxy)-2-adamantylidene)propene (38). By use of a previous procedure,[11] (E)-(1R)-(4(e)-hydroxy-2-adamantylidene)-propene (**37**) (8 mg, $[\alpha]^{26}_{Hg}$ +29.44 ± 1.67°, 84% ee) was benzoylated to yield after purification 10 mg of (E)-(1R)-(4(e)-(benzoyloxy)-2-adamantylidene)propene (**38**): $[\alpha]^{26}_{Hg}$ +21.94 ± 0.46° (c 0.29, $CHCl_3$); IR ($CHCl_3$) 2920, 2860, 1718, 1650, 1590, 1470, 1460, 1350, 1325, 1286, 1128, 1020-910 cm^{-1}; ^1H NMR δ 1.60-2.40 (m, 10 H), 2.67 (br s, 1 H), 3.03 (br s, 1 H), 5.02 (dd, J = 1.97, 10.20 Hz, 1 H), 5.12 (br s, 1 H), 5.17 (dd, J = 1.51, 16.10 Hz, 1 H), 5.90 (d, J = 11 Hz, 1 H), 6.61 (sextet, J = 10.45, 10.62, 16.82 Hz, 1 H), 7.40-7.60 (m, 3 H), 8.10 (m, 2 H); UV (c 2.58 × 10^{-5}, 2.58 × 10^{-4}, cyclohexane) λ_{279} ε 790, λ_{271} ε 980, λ_{247} ε 16 500, λ_{238} ε 28 500, λ_{232} ε 29 400, λ_{195} ε 37 600; CD (c 2.58 × 10^{-4}, 2.58 × 10^{-3}, cyclohexane) $\Delta\epsilon_{279}$ +0.14, $\Delta\epsilon_{271}$ +0.28, $\Delta\epsilon_{238}$ +15.78, $\Delta\epsilon_{220}$ -9.98. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.63; H, 7.48. Found: C, 81.66; H, 7.71.

Acknowledgment. We thank Prof. J. Brewster, Purdue University, who, serving as a referee, made substantial contributions to the clarity of this article. We are indebted to him. This work was supported by a grant from the National Science Foundation, to whom we are grateful.

Characterization of the Copper Sites in *Pseudomonas perfectomarina*[1] Nitrous Oxide Reductase by Resonance Raman Spectroscopy

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Abstract: Several unusual copper chromophores are observed in various forms of *Pseudomonas perfectomarina* nitrous oxide reductase. Resonance Raman spectroscopy at 290 and 77 K has been used to characterize some of the copper sites in the resting and reduced forms of this enzyme. Eleven to twelve fundamentals are observed at 77 K with 514.5-nm excitation, consistent with resonance enhancement for both metal-ligand stretches and internal ligand deformations. Comparisons to resonance Raman spectra of blue (type 1) copper proteins and Cu(II)-substituted liver alcohol dehydrogenase indicate that the 540-nm chromophore of resting N_2O reductase likely is associated with a $Cu^{II}S_2(cys)_2N(his)$ site. No evidence was found for contributions from Cu^{II}-tyrosine units or from an organic coenzyme to the visible absorption spectra. The low-activity resting form contains a copper site that displays a resonance Raman spectrum similar to those observed for blue copper sites; the high-activity form apparently does not contain such a site. Variations in the enzymatic activity of resting N_2O reductase may correlate with the number of 540-nm chromophores present. When either resting form is reduced by ascorbate or dithionite, new blue forms ($\lambda_{max} \simeq 650$ nm) are produced. Reduced N_2O reductase displays a resonance Raman spectrum that is, at least, very similar to that of the low-activity resting form obtained with 633-nm excitation. The circular dichroism spectrum of reduced N_2O reductase resembles the CD spectra of several blue copper proteins, with regard to band energies and intensities. It is likely that reduced N_2O reductase contains an oxidized copper site that is inaccessible to external, anionic reductants.

Denitrification is the reduction of nitrate to dinitrogen, as schematically illustrated below:[3]

$$2NO_3^- \rightarrow 2NO_2^- \rightarrow 2NO \rightarrow N_2O \rightarrow N_2 \qquad (1)$$

Although important to balancing the global nitrogen cycle, denitrification is a biologically (and economically) expensive process, since it returns fixed nitrogen (nitrate is readily reduced to ammonia by many organisms) to the atmosphere. Recently, certain

(1) Transfer of *Pseudomonas perfectomarina* to *Pseudomonas stutzeri* has recently been proposed. See: Döhler, K.; Huss, V. A. R.; Zumft, W. G. *Int. J. Syst. Bacteriol.* **1987**, *37*, 1-3.

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0002-7863/87/1509-6730$01.50/0