mixture. The eluant was concentrated under reduced pressure to give 0.16 g (74.5%) of **2** as an oil, which crystallized on standing: mp 52.5–54 °C; $[\alpha]_D$ −136.7° (*c* 0.33, benzene) [lit.[4c] $[\alpha_D]$ −134° (*c* 0.35, benzene)]. This material was determined to be optically pure by chiral HPLC analysis on a Chiralcel OJ column. The spectroscopic properties of **2** were identical with those reported in the literature.[4a]

Chiral Recognition of Asymmetric Amine Salts by Chemically Modified Polyether Antibiotics

Hiroshi Tsukube* and Hajime Sohmiya[1]

Department of Chemistry, College of Liberal Arts & Science, Okayama University, Okayama 700, Japan

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The most striking feature of polyether antibiotics is their ability to form stable complexes with alkali and alkaline earth metal cations. They are known to accommodate guest metal cations in their pseudo-cyclic cavities and to transport them selectively across the biomembrane.[2] Since they are composed of a number of optically active segments, they may provide chiral and ordered pseudo-cavities that specifically accommodate certain enantiomerically pure ammonium cations as well as some metal cations. Westley et al. first applied naturally occurring lasalocid to the preferential crystallization of salts with racemic amines.[3] More recently, Maruyama et al. demonstrated that some monensin amide derivatives exhibit enantiomer selectivity for several chiral ammonium cations comparable to those with chiral crown ethers.[4] Although only a limited number of successful examples have been reported, these findings clearly offer the interesting possibility that a new series of chiral host molecules may be derivable from natural polyether antibiotics.

We prepared a new series of chiral host molecules **1c–e**, **2b**, **3b**, and **4b** from natural monensin (**1a**), lasalocid (**2a**), salinomycin (**3a**), and nigericin (**4a**) (Chart I). Although the polyether antibiotics employed are themselves incapable of discriminating between optical isomers of chiral amine salts, some modified materials formed diastereomeric complexes with chiral amine salts and exhibited potential enantiomer selectivity in the electrochemical sensory system.

Results and Discussion

We obtained various ester derivatives of polyether antibiotics in 80–98% yields by cryptand[2.2.2]-promoted reaction with the corresponding bromides.[5] Their guest-binding properties were characterized by ion-selective electrode techniques.[6] The enantiomer selectivity coefficient $K_{S,R}$ is defined as $10^{(E_S-E_R)/0.059}$ (at 25 °C), where E_S and E_R represent the potentials to the *S*- and *R*-guest

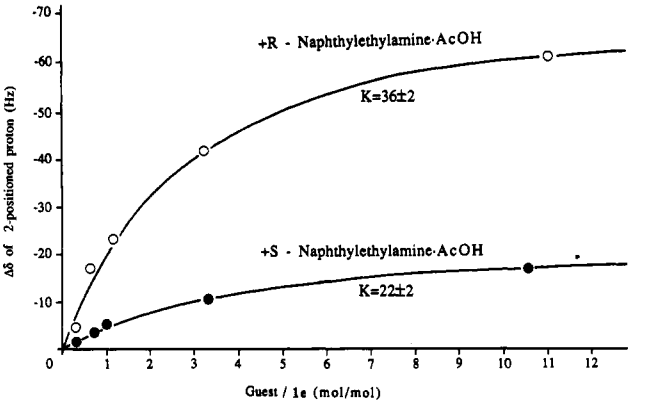

Figure 1. ^{1}H NMR (500 MHz) titration curves of monensin pentafluorobenzyl ester (**1e**) with (*S*)- and (*R*)-naphthylethylamine·AcOH. Concentration of **1e**: 0.0146 M in $CDCl_3$.

containing solutions. This selectivity coefficient should correlate with the stability constants of the complexes between the employed ionophore and optically active ammonium cations in the membrane.[7] Typical results are summarized in Table I.

The sensor electrodes incorporating the parent and modified polyether antibiotics generally exhibited near Nernstian responses for chiral ammonium salts in the range of 1×10^{-1} to 1×10^{-4} mol/L. Although some of them had been employed as specific ionophores of certain metal cations,[8] they also formed stable complexes with primary ammonium cations. Interestingly, chemically modified polyether antibiotics **1b–e**, **2b**, **3b**, and **4b** showed chiral recognition behavior toward some chiral ammonium cations, while natural antibiotics **1a**, **2a**, **3a**, and **4a** having carboxylic acid moieties exhibited little discrimination between these enantiomers. The enantiomer selectivity coefficients $K_{S,R}$ are largely dependent on the structures of the parent polyether antibiotics. In particular, monensin derivatives **1b–e** showed excellent chiral recognition ability; the potential differences for phenylglycine ester salt (Ph-GlyOMe·HCl), $E_S - E_R$, reached the relatively high values of 33–38 mV, and enantiomer selectivity coefficients $K_{S,R}$ were calculated as 3.7–4.4. Monensin lactone (**1f**)[9] and nonactin (**5a**) with similar chiral polyether linkages and ester groups in the macrocyclic skeletons were also examined for comparison. Since they show low enantiomer selectivity coefficients, monensin ester derivatives **1b–e** are believed to have neutral, acyclic (but pseudo-cyclic) polyether skeletons suitable for chiral recognition of asymmetric ammonium cations.

The enantiomer-selective complexation behavior of monensin ester derivatives was investigated by 500-MHz ^{1}H NMR spectroscopy. Table II summarizes guest-induced ^{1}H NMR spectral changes of several monensin derivatives. For example, the addition of (*R*)-naphthylethylamine salt to a $CDCl_3$ solution of monensin ester **1e** caused shifts of the signals for several protons attached to the carbons surrounding the pseudo-cavity, such as those positioned at 2, 5, 20, 21, and 31. These observations strongly suggest that the guest ammonium cation is located at the center of the pseudo-cavity of monensin ester and effectively interacts with several oxygen atoms. Its *S* isomer showed definite but different spectral changes.

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Table I. Enantiomer Selectivity Coefficients ($K_{S,R}$) of Naturally Occurring Ionophores and Their Esters

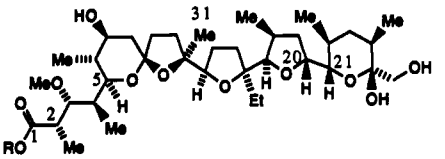
	$K_{S,R}$[a]					
ionophore	Ph-GlyOMe·HCl	PheOMe·HCl	LeuOMe·HCl	ProOMe·HCl	naphthylethylamine·HCl	phenethylamine·HCl
1a	1.8	1.6	1.6	1.0	0.76	0.79
1b	3.7	2.1	2.4	0.90	0.47	0.54
1c	4.0	2.2	2.5	0.77	0.48	0.56
1d	4.4	2.7	3.1	0.91	0.36	0.49
1e	4.4	2.5	3.4	1.0	0.37	0.53
2a	1.2	1.1	1.1	1.0	1.0	0.96
2b	1.8	1.3	1.5	0.82	0.73	0.87
3a	1.4	1.1	1.2	1.2	0.91	1.0
3b	1.7	1.2	1.3	1.0	0.83	0.75
4a	1.0	1.0	1.0	1.1	1.0	0.93
4b	1.1	1.8	1.6	1.0	1.0	1.3
5a	1.2	1.1	1.1	1.0	1.0	0.96
1f	1.0	1.0	1.0	1.0	1.1	1.0

[a] Reproducibility ±0.3.

Table II. Guest-Induced Changes in ^{1}H NMR Chemical Shift Values of 1a, 1b, 1d, and 1e

			$\Delta\delta$ (Hz)[c]				
ionophore[a]	guest·AcOH (1 equiv to ionophore)	$K_{S,R}$[b]	H-C_2[d]	H-C_5[d]	H-C_{20}[d]	H-C_{21}[d]	H-C_{31}[d]
1a	(*R*)-naphthylethylamine	0.76	−4.1	+6.5	+1.4	+2.0	+1.4
	(*S*)-naphthylethylamine		−4.2	+6.2	+1.5	+2.1	+1.6
	(*R*)-phenethylamine	0.79	−3.0	+6.0	+1.7	+1.9	+2.0
	(*S*)-phenethylamine		−2.2	+6.8	+2.2	+2.3	+2.5
1b	(*R*)-naphthylethylamine	0.47	−10.8	−6.5	+8.4	−7.2	−10.9
	(*S*)-naphthylethylamine		−2.4	+3.8	+1.6	−3.5	+5.5
	(*R*)-phenethylamine	0.54	−4.2	−1.8	+5.1	−3.4	−4.8
	(*S*)-phenethylamine		+0.7	+4.6	+0.2	−1.3	+1.3
1d	(*R*)-naphthylethylamine	0.36	−16.7	−7.8	+10.3	−11.9	−16.5
	(*S*)-naphthylethylamine		−4.8	+4.5	+2.5	−1.7	+5.4
	(*R*)-phenethylamine	0.49	−11.3	−4.6	+1.6	−6.3	−9.6
	(*S*)-phenethylamine		−4.8	+1.2	−2.4	−4.5	−2.1
1e	(*R*)-naphthylethylamine	0.37	−24.7	−9.2	+9.8	−12.2	−17.9
	(*S*)-naphthylethylamine		−7.9	+2.1	+1.4	−5.0	+2.5
	(*R*)-phenethylamine	0.53	−11.6	−3.2	+5.3	−5.3	−6.9
	(*S*)-phenethylamine		+0.8	+3.1	+0.7	−2.0	+0.6

[a] Concentration: 0.0146 M in $CDCl_3$. [b] Electrochemical enantiomer selectivity coefficient (see Table I). [c] Reproducibility; maximum ±2.9 Hz. "+" and "−" indicate higher and lower field shifts, respectively. [d] H-C_n indicates the proton attached to *n*-positioned carbon. ^{1}H NMR chemical shift values for H-C_2, H-C_5, H-C_{20}, H-C_{21}, and H-C_{31} of **1a** and **1e** were as follows: **1a**, 2.54, 4.03, 4.40, 3.83, and 1.50; **1e**, 2.69, 4.03, 4.29, 3.82, and 1.37 ppm, respectively. Numbering of carbon atoms is shown below.



Since the shifted values of proton signals positioned at carbons 5 and 31 interestingly exhibit the opposite sign to the *R* isomer induced signals, monensin ester **1e** evidently forms encapsulated and enantiomer-selective complexes with these chiral guest ammonium cations.[10]

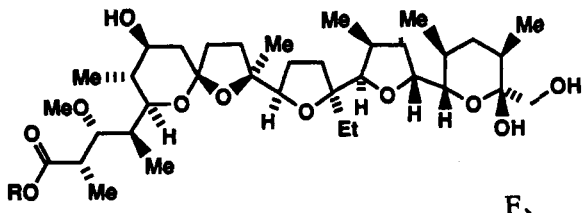
Figure 1 illustrates plots of the guest-induced changes in chemical shifts of the proton signal positioned at carbon 2 with changes in the concentration ratio of (*S*)- or (*R*)-naphthylethylamine acetate to monensin ester **1e**. These plots gave good fits for 1:1 complexes with thermodynamic stability constants K = 36 L/mol for the *R* isomer and 22 L/mol for the *S* isomer.[11] Similar spectral changes were observed with other monensin derivatives and chiral ammonium cations. Clearly, a combination of monensin derivative and guest amine salt that exhibited large spectral changes provides excellent enantiomer selectivity in the electrochemical sensory system. In contrast, naturally occurring monensin (**1a**) showed almost the same spectral changes in the presence of *R* and *S* guest ammonium cations.[12] Since large shifts were only observed in the signals for protons attached to carbons 2 and 5, the guest ammonium cation appears to be in loose contact with the chiral polyether skeleton in the complex. Electrostatic interaction between the terminal carboxylate anion of monensin and the guest ammonium cation may be significantly involved. These electrochemical and spectroscopic studies strongly suggest that monensin ester derivatives provide encapsulated complexes in which guest ammonium cations are comfortably included by the chiral and pseudo-cyclic polyether skeleton of monensin. Further

(10) We took NOESY spectra of the monensin ester **1e** and (*R*)- or (*S*)-naphthylethylamine–AcOH system, but did not find a definite NOE correlated peak (JEOL FX-400 400 MHz, [**1e**] = [amine·AcOH] = 0.0292 mol/L, mixing time 500 ms).

(11) We also calculated stability constants (K) based on changes of other proton signals and obtained similar values. For example, K was estimated as 42 ■ 10 L/mol for monensin **1e**–(*R*)-naphthylethylamine–AcOH from induced shifts of H-C_{31} proton.

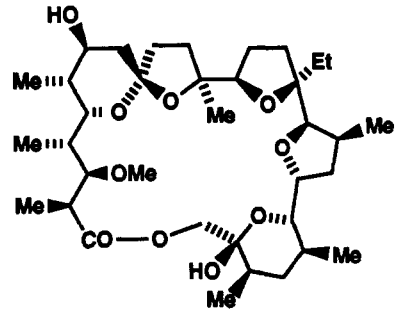
(12) Although the shifted values were too small to determine the stoichiometry and stability constants, monensin stoichiometrically extracted several ammonium salts into $CHCl_3$ from aqueous solution.

Chart I. Naturally Occurring Ionophores and Their Esters

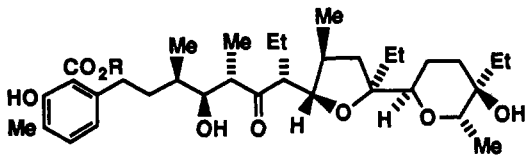


1a : R= Na
1b : R= CH_3
1c : R= CH_2-Ph

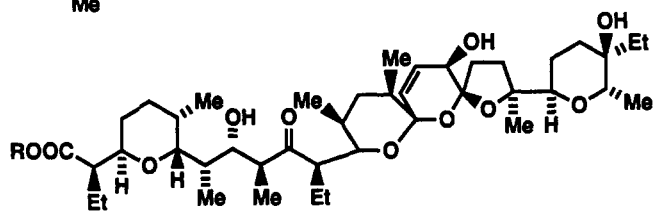
1d : R= CH_2-(4-F-Ph)
1e : R= CH_2-(F_5-Ph)



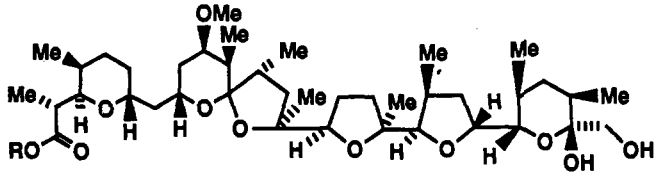
1f



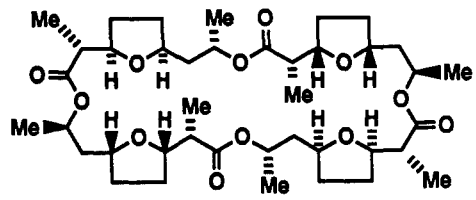
2a : R= Na
2b : R= CH_2-Ph



3a : R= Na
3b : R= CH_2-Ph



4a : R= Na
4b : R= CH_2-Ph



5a

chemical modification of naturally occurring polyether antibiotics may offer a promising method for the development of new and specific chiral host molecules.

Experimental Section

Materials. The ionophores employed were obtained as follows: monensin (**1a**) and its methyl ester **1b** (Calbiochem); lasalocid (**2a**) (Sigma); salinomycin (**3a**) (Wako); nigericin (**4a**) (Calbiochem); and nonactin (**5a**) (Fluka). These are all "hazardous compounds" and require careful handling. Monensin lactone (**1f**) was prepared by the procedure in the literature.[9] Other ester derivatives were obtained from sodium salts of polyether antibiotics and the corresponding bromides. A typical synthetic procedure was as follows.[5] In the presence of cryptand[2.2.2] (50 mg), monensin sodium salt (50 mg) was treated with benzyl bromide (100 mg) in CH_3CN at room temperature for 1 day. Chromatography (silica gel, $CH_2Cl_2/CH_3CO_2C_2H_5$) gave monensin benzyl ester (**1c**) (54 mg). The same procedure was used for the synthesis of the other ester derivatives. All ester derivatives were confirmed as pure materials by TLC analysis (Merck kieselgel 60 F_{254}, $CH_3CO_2C_2H_5/CH_2Cl_2$ = 1:4, v/v). They were fully characterized by ^1H NMR, ^{13}C NMR, IR, and high resolution FAB-mass spectroscopies. Assignments for ^1H NMR and ^{13}C NMR signals of **1c–e** and **2b** were based on previous reports,[13] while those of **3b** and **4b** were characterized by comparison with those of parents **3a** and **4a**. In ^1H NMR spectra of **2b** and **4b**, some signals of hydroxy protons were not observed. Selected spectroscopic data for new compounds are as follows.

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Monensin benzyl ester (1c): IR ($CHCl_3$) 1720 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.85–2.27 (identical with parent monensin, 45 H), 2.67 (br s, 1 H), 2.71 (m, 1 H), 3.25 (s, 3 H), 3.46 (m, 2 H), 3.59 (m, 2 H), 3.76 (m, 1 H), 3.80 (dd, 1 H, J = 3.1, 10.0 Hz), 3.86 (d, 1 H, J = 4.7 Hz), 3.88 (br s, 1 H), 4.05 (dd, 1 H, J = 2.3, 9.1 Hz), 4.28 (m, 1 H), 4.38 (d, 1 H, J = 9.3 Hz), 5.14 (d, 1 H, J = 12.4 Hz), 5.20 (d, 1 H, J = 12.3 Hz), 7.30–7.39 (m, 5 H); FAB-HRMS (m/e) calcd for $C_{43}H_{68}O_{11}$ - $2H_2O$ + H 725.4629, found 725.4692.

Monensin *o*-fluorobenzyl ester (1d): IR ($CHCl_3$) 1710 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.84–2.28 (identical with parent monensin, 45 H), 2.70 (m, 1 H), 2.79 (br s, 1 H), 3.25 (s, 3 H), 3.46 (br s, 2 H), 3.57 (m, 2 H), 3.74 (m, 1 H), 3.81 (dd, 1 H, J = 3.0, 10.0 Hz), 3.87 (d, 1 H, J = 4.7 Hz), 4.00 (br s, 1 H), 4.05 (dd, 1 H, J = 2.5, 8.9 Hz), 4.28 (m, 1 H), 4.43 (d, 1 H, J = 8.9 Hz), 5.20 (d, 1 H, J = 12.7 Hz), 5.26 (d, 1 H, J = 12.2 Hz), 7.06 (m, 1 H), 7.13 (m, 1 H), 7.28–7.32 (m, 1 H), 7.43 (m, 1 H); FAB-HRMS (m/e calcd for $C_{43}H_{67}O_{11}F$ + Na 801.4565, found 801.4445.

Monensin pentafluorobenzyl ester (1e): IR ($CHCl_3$) 1720 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.84–2.28 (identical with parent monensin, 45 H), 2.69 (m, 1 H), 2.72 (br s, 1 H), 3.29 (s, 3 H), 3.46 (br s, 2 H), 3.56–3.60 (m, 2 H), 3.75 (m, 1 H), 3.82 (dd, 1 H, J = 3.2, 9.8 Hz), 3.88 (d, 1 H, J = 4.5 Hz), 4.03 (dd, 1 H, J = 2.3, 9.0 Hz), 4.04 (br s, 1 H), 4.29 (m, 1 H), 4.44 (br s, 1 H), 5.25 (s, 2 H); FAB-HRMS (m/e) calcd for $C_{43}H_{63}O_{11}F_5$ + Na 873.4188, found 873.4233.

Lasalocid benzyl ester (2b): IR ($CHCl_3$) 1650, 1700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.76–2.25 (identical with parent lasalocid, 36 H), 2.20 (s, 3 H), 2.77–2.88 (m, 4 H), 3.19 (d, 1 H, J = 2.2 Hz), 3.42 (br s, 1 H), 3.44 (dd, 1 H, J = 2.2, 11.9 Hz), 3.74–3.84 (m, 3 H), 5.39 (d, 1 H, J = 12.1 Hz), 5.41 (d, 1 H, J = 11.9 Hz), 6.64 (d, 1 H, J = 7.5 Hz), 7.14 (d, 1 H, J = 7.9 Hz), 7.34–7.45 (m, 5 H); FAB-HRMS (m/e) calcd for $C_{41}H_{60}O_8$ + H 681.4366, found 681.4357.

Salinomycin benzyl ester (3b): IR ($CHCl_3$) 1700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.68–2.43 (identical with parent salinomycin, 50 H), 1.42 (s, 3 H), 2.20 (m, 1 H), 2.39 (m, 1 H), 2.44 (br s, 1 H), 2.74 (m, 1 H), 3.00 (d, 1 H, J = 5.6 Hz), 3.05 (m, 1 H), 3.18 (m, 1 H), 3.59 (dd, 1 H, J = 2.6, 10.4 Hz), 3.67 (br t, 1 H, J = 9.3 Hz), 3.82 (q, 1 H, J = 6.9 Hz), 3.90 (d, 1 H, J = 9.3 Hz), 4.00 (br d, 1 H, J = 8.9 Hz), 4.06 (dd, 1 H, J = 5.3, 5.9 Hz), 4.12 (m, 1 H), 5.34 (d, 1 H, J = 12.4 Hz), 5.39 (d, 1 H, J = 12.6 Hz), 5.98 (br d, 1 H, J = 10.7 Hz), 6.08 (dd, 1 H, J = 2.1, 10.7 Hz), 7.28–7.45 (m, 5 H); FAB-HRMS (m/e) calcd for $C_{49}H_{76}O_{11}$ - H_2O + H 823.5360, found 823.5369.

Nigericin benzyl ester (4b): IR ($CHCl_3$) 1720 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.86–2.55 (identical with parent nigericin, 53 H), 3.27 (m, 1 H), 3.33 (s, 3 H), 3.52–3.60 (m, 3 H), 3.79 (dd, 1 H, J = 2.1, 10.5 Hz), 3.84 (m, 1 H), 3.90 (d, 1 H, J = 4.2 Hz), 4.23 (m, 1 H), 4.31 (m, 1 H), 4.95 (br s, 1 H), 5.10 (d, 1 H, J = 12.5 Hz), 5.23 (d, 1 H, J = 12.5 Hz), 7.29–7.37 (m, 5 H); FAB-HRMS (m/e) calcd for $C_{47}H_{74}O_{11}$ + K 853.4868, found 853.4847.

Ion-Selective Electrode Experiments. Electrode cells of the type Ag; AgCl, KCl(saturated)/0.3 M NH_4NO_3/sample solution/membrane/0.01 M NaCl, AgCl; Ag [membrane composition: 1 wt % potassium tetrakis(*p*-chlorophenyl)borate, 3 wt % ionophore, 30 wt % poly(vinyl chloride), 66 wt % dibenzyl ester] were used for electromotive force (emf) measurements. The membrane prepared was mounted on a DKK membrane electrode body to form an ion-selective electrode. Each emf was measured at pH = 3.0 ± 0.1 with an Orion Research EA 920 ion analyzer. The values obtained were set into the Nicolsky-Eisenman equation for calculation by the separate solution method.[14]

Method of Evaluation for Stability Constants. The stability constant (K) for 1:1 complexation is defined in eq 1, where

$$K = [C]/\{[I]_o - [C]\}\{[G]_o - [C]\} \quad (1)$$

$[C]$, $[I]_o$, and $[G]_o$ represent the concentration of complex in the equilibrated state, initial concentration of ionophore, and initial concentration of guest, respectively. Supposing that guest-induced change in the chemical shift of proton signal ($\Delta\delta$) can be related to $\Delta\delta_\infty$ (saturated $\Delta\delta$) as in eq 2. Thus, one can derive eq 3.

$$\Delta\delta = [C]\Delta\delta_\infty/[I]_o \quad (2)$$

$$\Delta\delta = [[I]_o + [G]_o + 1/K - \{([I]_o + [G]_o + 1/K)^2 - 4[I]_o[G]_o\}^{1/2}]/(2[I]_o/\Delta\delta_\infty) \quad (3)$$

Substituting measured $\Delta\delta$, $[I]_o$, and $[G]_o$ values in eq 3, we determined the stability constant (K) by nonlinear least-squares treatment (Gauss–Newton method). Curves indicated in Figure 1 were computer-calculated titration curves according to eq 3.

Acknowledgment. We are grateful to Professor Kazuhiro Maruyama of Kyoto University and Professor Tatsuo Higashiyama of Okayama University for valuable discussions. We also express our gratitude to the SC-NMR Laboratory of Okayama University for 500-MHz ^1H NMR experiments. This research was supported in part by Grants-in-Aid for Scientific Research on Priority Areas ("Multiplex Organic System") and for Encouragement of Young Scientists from the Ministry of Education, Science, and Culture, Japan. Financial support from Shimadzu Science Foundation is also appreciated.

Supplementary Material Available: ^1H and/or ^{13}C NMR spectra for compounds **1c–e**, **2b**, **3b**, and **4b** (20 pages). Ordering information is given on any current masthead page.

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1,4-Dimethyl-9,10-anthraquinodimethane: Molecular and Crystal Structure of a Simple Quinodimethane

Stuart Rosenfeld*

Department of Chemistry, Smith College, Northampton, Massachusetts 01063

Jerry P. Jasinski

Department of Chemistry, Keene State College, Keene, New Hampshire 03431

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Quinodimethanes have proven to be extremely useful intermediates for the synthesis of cyclophanes[1] and other compounds. Their propensity toward cyclodimerization, polymerization, and Diels–Alder chemistry,[2] while an advantage in synthetic applications, creates challenges for those engaged in structural studies. Nonetheless, numerous reports of the spectroscopic characteristics of these compounds at low temperatures, including electronic,[3] vibrational,[3] nuclear magnetic resonance,[4] and photoelectron[5] spectroscopy, have appeared. Theoretical approaches, particularly molecular orbital calculations, have also amplified understanding of the chemistry and structure of these labile molecules.[6] A number of isolable 9,10-anthraquinodimethanes, e.g., **1**[7] and **2**,[8,9] have been

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