Pergamon

Tetrahedron, Vol. 53, No. 20, pp. 6817-6824, 1997
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00323-2

Substituent Effect on the Selectivity of [3.3]Orthoanthracenophanes in the Diels-Alder Reaction with *N*-(*p*-Substituted phenyl)maleimides

Shuntaro Mataka,*[a] Jiang Ma,[b] Thies Thiemann,[c] Takao Mimura,[a] Tsuyoshi Sawada,[a] and Masashi Tashiro[a]

[a]Institute of Advanced Material Study, [b]Department of Molecular Science and Technology, Graduate School of Engineering Sciences, Kyushu University, 6-1, Kasuga-koh-en, Kasuga-shi, Fukuoka 816, Japan

[c]Institut für Organische Chemie, Universität Hamburg, Martin-LutherKing Platz 6, D-20146 Hamburg, Germany

Abstract: Diels-Alder reactions of benzo- and naphtho-[3.3]orthoanthracenophanes **1a-b** with *N*-(*p*-nitro, chloro or methoxy-substituted phenyl) maleimides **2a-c** were investigated. In most cases, approximately equal amounts of *inside*-adduct **3** and *outside*-adducts (**4** + **5**) were obtained, except for the *outside*-selective addition reaction of naphthophane **1b** with *p*-nitro derivative **2a**. Of the *outside*-adduct, the *endo*-adduct **4** was formed predominantly in all cases. Especially, the reaction of **1b** afforded *endo*-adducts **4ba-bc** almost exclusively. These facts suggest that the interaction between the phenyl group of **2** and the part of the anthraceno-unit closest to the underlying naphtho/benzo-moiety of **1** leads to a greater tendency toward *endo*-orientation. © 1997 Elsevier Science Ltd.

Introduction

[3.3]Orthoanthracenophanes **1a-b** are rigid molecules with opposing layered aromatic systems (**Fig. 1**). Previously it has been reported that orthophanes **1** exhibit a remarkable π-face diastereoselectivity in Diels-Alder (D-A) reactions.[1] In reactions with dimethyl acetylenedicarboxylate, dimethyl azodiformate, and *N*-phenyl-1,2,4-triazoline-2,5-dione, **1** shows a high *outside*-selectivity, while the reactions with maleic anhydride (MA)

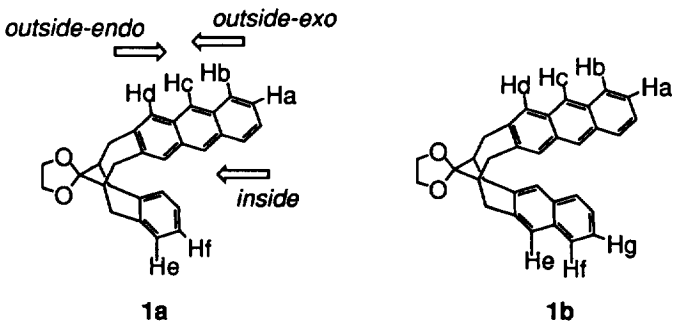


Figure 1 The structures of [3.3]orthoanthracenophanes **1a-b**.

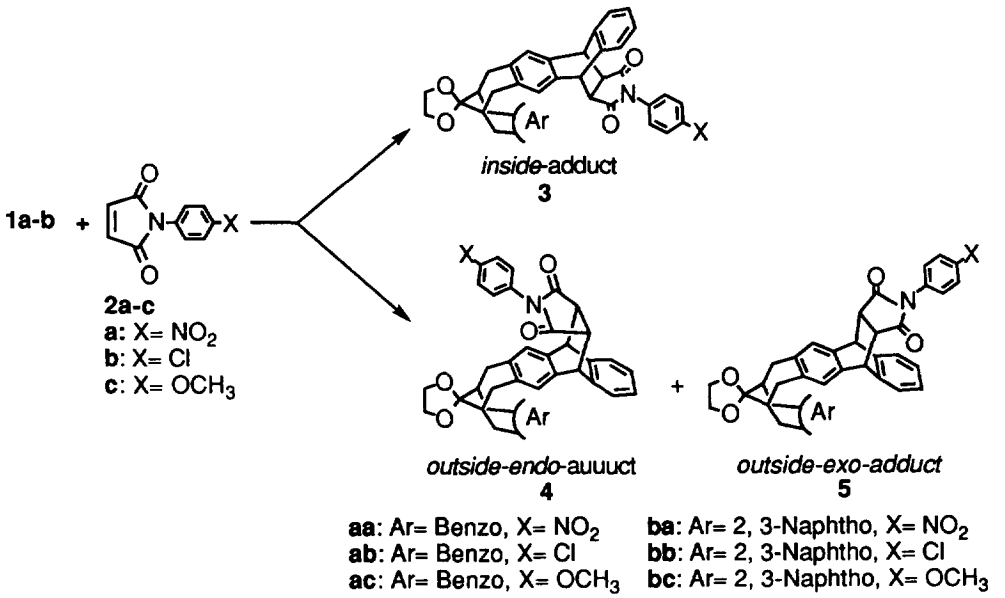
and maleimide (MI) proceed in an *inside*-face selective manner. A bulky substituent such as *N-tert*-butyl and *N*-phenyl on the maleimides decreases the *inside/outside*-facial selectivity. Furthermore, it is interesting to note that the D-A reaction of naphtho[3.3]orthoanthracenophane **1b** with *N*-phenylmaleimide (NPM) forms only one of the two possible isomeric *outside*-adducts. In this case, NPM attacks from the more congested side to produce the *outside-endo*-adduct. On the other hand, the reaction of **1b** with *N-tert*-butylmaleimide gives the *exo*-isomer as the major *outside*-adduct.[1] These results suggest that a through-space interaction between the stacked aromatic π-systems of **1** and the phenyl ring of NPM plays an important role in the orientation of the cycloaddend leading to an *endo-outside* addition. In order to investigate in more detail the steric and electronic contributions of the cycloaddend to this interesting selectivity of a "molecular cavity", the influence of the π-electron density and steric demand of different *N*-phenylmaleimides was studied.

We now report the substituent effect on the diastereoselectivities in D-A reactions of **1a-b** with *N*-(*p*-substituted phenyl)-maleimides **2a-c**.

Results and Discussion

Reactions and Assignment of Diastereomers

The Diels-Alder reactions of cyclophanes **1** with **2a-c** were carried out in benzene-d_6 at 110 °C in a sealed NMR sample tube and gave the cycloadducts in 80-98% yield (**Scheme 1** and **Table 1**). Pure *inside*-adducts **3** were obtained by HPLC separation from the reaction mixtures, while the *outside*-adducts were obtained as a mixture of *endo*- and *exo*-diastereoisomers **4** and **5**.



Scheme 1

Inside-adduct **3** can easily be distinguished from the corresponding *outside*-adducts **4** and **5**, on the basis of their ^{1}H NMR spectra, as described previously.[1b] The ring protons H_f and H_g of the naphtho-moiety of **4ba, 4bb, 4bc** and **5bc** are shielded by the ring current of the outer benzo-ring of dihydroanthraceno-unit and

thus shifted up-field as compared to the corresponding protons of **3ba**, **3bb**, and **3bc**. The *exo/endo*-assignment of the *outside*-adducts **4** and **5** was done on the basis of ^{1}H NMR spectra, NOE-experiments, and X-ray crystallographic analysis of the *endo*-adduct **4aa**.

The proton H_d of the *outside-endo* adduct **4aa**, **4ab**, and **4ac** exhibit a chemical shift of δ 6.46-6.52 ppm. The protons H_d of the *exo*-isomers **5aa**, **5ab**, and **5ac** show a chemical shift of δ 6.64-6.71 ppm, a down field shift of 0.12-0.18 ppm, as compared to the corresponding *endo*-isomer **4**. The up-field shift of H_d in the *endo*-adducts is considered to be due to the magnetic anisotropy of the carbonyl group of the maleimido-moiety.[2] An X-ray crystallographic analysis of the 1:1 complex of **4aa** and dichloromethane confirmed the *exo/endo*-assignments (**Fig. 2**). The *endo*-isomer is the major outside-diastereomer in the reaction.

Table 1. Diels-Alder reaction of **1** with NPM[a] and **2** at 110 °C

Phane	Dienophile	Total Yield of the Adducts (%)	Product Ratios	
			inside / outside	endo / exo
			3 / 4+5	**4 / 5**
1a	NPM	96	1 / 1	1.5 / 1
1a	**2a**	90	1 / 1.2	3 / 1
1a	**2b**	87	1 / 1.1	2 / 1
1a	**2c**	80	1 / 1.3	1.5 / 1
1b	NPM	96	1 / 1	1 / 0
1b	**2a**	86	1 / 2	1 / 0
1b	**2b**	87	1 / 0.9	1 / 0
1b	**2c**	82	1 / 1.2	5 / 1

a) Reference 1b.

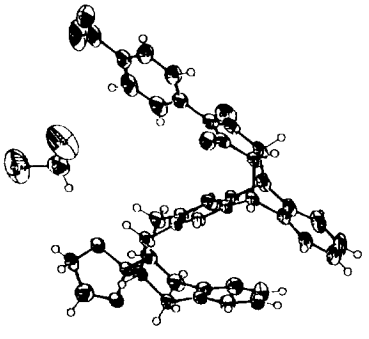
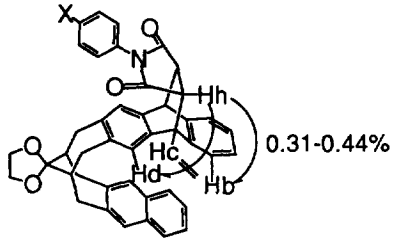


Figure 2 ORTEP Drawing of a 1:1 complex of **4aa** and dichloromethane



4ba-bc

Figure 3 NOE Experiments on *Outside-endo*-Adducts **4ba-bc**.

Naphthophane **1b** reacted with both **2a** and **2b** to give a single *outside*-adduct **4ba** and **4bb**, respectively. The protons H_d show a chemical shift of δ 6.75 ppm for **4ba** and 6.65 ppm for **4bb**, respectively. A mixture

of *outside*-adducts **4bc** and **5bc** formed in the reaction with **2c**. The major isomer **4bc** shows a sharp singlet at δ 6.63 ppm for the protons H_d. The signal of H_d of the minor isomer **5bc** appears at δ 6.98 ppm. The assignment of the stereochemistry of **4ba**, **4bb**, and **4bc** was further supported by NOE-experiments carried out at 50 °C using a 600 MHz NMR-spectrometer (in $CDCl_3$) (**Fig. 3**). When protons H_c of the 9,10-ethanoanthraceno-unit were irradiated, an NOE effect could be observed for the protons H_h (7.1-8.9%), H_d (5.5-6.9%), and H_b (5.6-8.0%). Irradiation of the protons H_h showed a small NOE effect on protons H_b (0.3-0.4%), but no effect on the signals of H_d.

Discussion

The ratios of the *inside*- to *outside*-adduct in the D-A reactions of **1** with *N*-(*p*-substituted phenyl)maleimides **2** are smaller in all cases than the ratio found in the same reaction with MI itself or MA.[1] Except for the reaction of naphthophane **1b** with **2a**, the *inside/outside*-ratios, as listed in in **Table 1**, are only slightly dependent upon the electronic nature of the substituent and are close to 1/1 observed in the reaction of **1b** with *N*-phenylmaleimide. Thus, these results can be explained in terms of steric repulsion in the transition state, leading to the *inside*-adduct **3**, between the bulky *p*-substituted phenyl group of dienophile **2** and the aromatic ring opposing the reaction site within the molecular cavity of **1**.

Of the *outside*-adducts, the *endo*-adducts **4** are formed predominantly in all cases. Especially, the reaction of naphthophane **1b** afforded *endo*-adducts **4ba**, **4bb**, and **4bc** almost exclusively, in marked contrast to the results obtained for the cycloaddition of **1b** with *N-tert*-butylmaleimide, where a slight *exo*-selectivity was noted.[1] These facts imply that the diastereoselectivity of D-A reaction of **2** on the *outside*-face of **1** is governed by electronic rather than steric factors. Furthermore, the *endo/exo*-ratio is markedly dependent on the electronic nature of the substituent of **2**. Thus, the reaction of **2a** with the strongly electron-withdrawing nitro group shows more *endo*-selectivity than the reaction of **2c** with the electron-donating methoxy-group. The relative order of *endo*-selectivity as a function of *p*-substituents of the phenylmaleimides can be listed as follows:

$$-NO_2 > -Cl > -H > -OCH_3$$

Attack of **2** from the more hindered *endo*-side of **1** leads to a transition state in which the phenyl group of the maleimide interacts with the aromatic system of the (former) anthraceno-unit closest to the underlying naphtho/benzo-moiety. This π–π interaction [3-10] between the phenyl ring and the most closely stacked aromatic part of the dienes **1**, as well as the secondary orbital interaction with the maleimide dienophiles, is assumed to be the governing factor for this *endo-outside*-selectivity. A second possible interaction between the maleimido-substituents and one of the lone-pairs of the oxygen of the acetal bridge is discounted as a dominant factor, as the diastereoselectivites exhibited by **1a** and **1b** are quite different. Thus, it has been shown that the through-space interaction between the opposing aromatic systems of the anthracenonaphthophane **1b** is larger than that of anthracenobenzophane **1a**. Indeed, larger *endo*-selectivities are observed for the cycloadditions of **2** with **1b** than with **1a**. Also, electron-withdrawing substituents on the phenyl-maleimides should favor the π–π-interaction and thus increase the *endo*- over *exo*-diastereoselectivity as found experimentally.

In conclusion, molecules **1** with an inner molecular cavity defined by two facing aromatic systems have been found to exhibit intriguing diastereoselectivities in D-A reactions. The π–π interaction of the aromatic units of these dienes do not only influence the *inside/outside*-selectivity of the molecules, but have been shown to have a dominant effect on the *exo/endo*-selectivity of the *outside*-addition.

Experimental

General: Melting points are uncorrected. Infrared spectra were obtained in KBr pellets. ^{1}H NMR were recorded at 270 MHz. CD_2Cl_2 was served as a solvent. Difference NOE spectra were obtained on a 600 MHz NMR spectrameter. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS 700 instrument (EI, 70eV). HPLC was carried out on a JASCO 880 HPLC (Develosil Packed Column :Φ 25 mm/250 mm). Benzene-d_6 (d-purity of 99.6%, Aldrich Co.) was used as supplied.

General procedure for the Diels-Alder reaction of 1a with 2a. A solution of **1a** (10 mg, 0.02 mmol) and **2a** (5 mg, 0.02 mmol) in benzene-d_6 (1 ml) was heated in a sealed NMR sample tube at 110 °C for 20 h. The solvent was evaporated in vacuo and HPLC of the residue with dichloromethane gave **3aa** (7 mg, 45%) and a mixture (7 mg, 45%) of **4aa and 5aa**. **Adduct 3aa**: mp 333-334 °C; colorless needles (dichloromethane); IR 2960, 2920, 1711, 1529, 1346, 1261, 1099, 803 cm^{-1}; ^{1}H NMR 2.33 (2H, brs.), 2.70-2.78 (4H, m), 3.22-3.24 (2H, m), 3.38-3.49 (4H, m), 4.08 (4H, s), 4.56 (2H, s), 6.72-6.73 (6H, m), 6.78-6.79 (2H, m), 7.09-7.16 (2H, m), 7.17-7.21 (2H, m), 8.11-8.15 (2H, m); HRMS calcd $C_{39}H_{32}N_2O_6$ 624.2260, found 624.2242. **Mixture of 4aa and 5aa**: mp 330 °C (decomp.); colorless needles (dichloromethane); IR 2916, 2882, 1719, 1522, 1494, 1377, 1344, 1187, 1175, 1103, 853, 744 cm^{-1}; HRMS calcd $C_{39}H_{32}N_2O_6$ 624.2260, found 624.2250. ^{1}H NMR of **4aa**: 2.24 (2H, brs.), 2.52-2.68 (4H, m), 3.26-3.43 (4H, m), 4.06 (6H, s), 4.52 (2H, s), 5.47-5.51 (2H, m), 6.24-6.27 (2H, m), 6.53 (2H, s), 6.63-6.66 (2H, m), 7.26-7.29 (2H, m), 7.41-7.44 (2H, m), 8.07-8.10 (2H, m). ^{1}H NMR of **5aa**: 2.24 (2H, brs.), 2.52-2.68 (4H, m), 3.26-3.43 (6H, m), 4.06 (4H, s), 4.52 (2H, s), 5.47-5.51 (2H, m), 6.24-6.27 (2H, m), 6.63-6.66 (2H, m), 6.71 (2H, s), 7.26-7.29 (2H, m), 7.41-7.44 (2H, m), 8.07-8.10 (2H, m).

Adducts 3ab, 4ab, and 5ab. The general procedure was followed, reacting **1a** (10 mg, 0.02 mmol) and **2b** (5 mg, 0.02 mmol) for 20 h. HPLC of the residue with dichloromethane gave **3ab** (6 mg, 40%) and a mixture (7 mg, 47%) of **4ab** and **5ab**. **Adduct 3ab**: mp 239 °C (decomp.); colorless prisms (dichloromethane); IR 2956, 2918, 1714, 1494, 1392, 1194, 1102, 811, 756, 747 cm^{-1}; ^{1}H NMR: 2.32 (2H, brs.), 2.65-2.78 (4H, m), 3.18-3.19 (2H, m), 3.34-3.48 (4H, m), 4.08 (4H, s), 4.53 (2H, s), 6.44-6.48 (2H, m), 6.63-6.71 (6H, m), 7.09-7.12 (2H, m), 7.16-7.19 (2H, m), 7.24-7.29 (2H, m); HRMS calcd for $C_{39}H_{32}ClNO_4$ 613.2020 and 615.2014, found 613.2028 and 615.1989. **Mixture of 4ab and 5ab**: mp 321-323 °C; colorless rhombic crystals (dichloromethane); IR 2916, 1719, 1493, 1390, 1194, 1090, 744 cm^{-1}; HRMS calcd for $C_{39}H_{32}ClNO_4$ 613.2020 and 615.2014, found 613.2025 and 615.1994. ^{1}H NMR of **4ab**: 2.24 (2H, brs.), 2.50-2.68 (4H, m), 3.21-3.42 (6H, m), 4.06 (4H, s), 4.49 (2H, s), 5.47-5.50 (2H, m), 6.23-6.27 (2H, m), 6.28-6.31 (2H, m), 6.52 (2H, s), 7.18-7.21 (2H, m), 7.24-7.26 (2H, m), 7.39-7.43 (2H, m). ^{1}H NMR of **5ab**: 2.24 (2H, brs.), 2.50-2.68 (4H, m), 3.21-3.42 (6H, m), 4.06 (4H, s), 4.49 (2H, s), 5.47-5.50 (2H, m), 6.23-6.27 (2H, m), 6.28-6.31 (2H, m), 6.66 (2H, s), 7.18-7.21 (2H, m), 7.24-7.26 (2H, m), 7.39-7.43 (2H, m).

Adducts 3ac, 4ac, and 5ac. The general procedure was followed, reacting **1a** (10 mg, 0.02 mmol) and **2c** (5 mg, 0.02 mmol) for 20 h. HPLC of the residue with dichloromethane gave **3ac** (6 mg, 40%) and a mixture (6 mg, 40%) of **4ac and 5ac**. **Adduct 3ac**: mp 308 °C (decomp.); colorless prisms (dichloromethane); IR 2918, 2882, 1713, 1513, 1396, 1253, 1103, 813, 746 cm^{-1}; ^{1}H NMR: 2.32 (2H, brs.), 2.65-2.78 (4H, m),

3.16-3.17 (2H, m), 3.33-3.48 (4H, m), 3.67 (3H, s), 4.08 (4H, s), 4.53 (2H, s), 6.34-6.37 (2H, m), 6.63-6.71 (6H, m), 6.77-6.81 (2H, m), 7.10-7.13 (2H, m), 7.14-7.20 (2H, m); HRMS calcd for $C_{40}H_{35}NO_5$ 609.2515, found 609.2516. **Mixture of 4ac and 5ac**: colorless rhombic crystals (dichloromethane): mp 349 °C (decomp.); IR 2882, 1713, 1513, 1396, 1252, 1103, 746 cm^{-1}; HRMS calcd for $C_{40}H_{35}NO_5$ 609.2515, found 609.2510. ^1H NMR of **4ac**: 2.25 (2H, brs.), 2.52-2.78 (4H, m), 3.19 (2H, s), 3.25-3.49 (4H, m), 3.69 (3H, s), 4.07-4.09 (4H, m), 4.49 (2H, s), 5.48-5.50 (2H, m), 6.19-6.28 (4H, m), 6.52 (2H, s), 6.74-6.79 (2H, m), 7.21-7.30 (2H, m), 7.38-7.42 (2H, m). ^1H NMR of **5ac**: 2.25 (2H, brs.), 2.52-2.78 (4H, m), 3.13 (2H, s), 3.25-3.49 (4H, m), 3.72 (3H, s), 4.07-4.09 (4H, m), 4.49 (2H, s), 5.48-5.50 (2H, m), 6.19-6.28 (4H, m), 6.64 (2H, s), 6.74-6.79 (2H, m), 7.21-7.30 (2H, m), 7.38-7.42 (2H, m).

Adducts 3ba and 4ba. The general procedure was followed, reacting **1b** (10 mg, 0.02 mmol) and **2a** (5 mg, 0.02 mmol) for 20 h. HPLC of the residue with dichloromethane gave **3ba** (5 mg, 33%) and **4ba** (8 mg, 53%). **Adduct 3ba**: mp 334-335 °C; colorless prisms (ethanol); IR 2962, 2918, 1721, 1523, 1342, 1261, 1100, 1022, 802 cm^{-1}; ^1H NMR: 1.73 (2H, s), 2.43 (2H, brs.), 2.75-3.02 (4H, m), 3.39-3.66 (4H, m), 4.12 (4H, s), 4.25 (2H, s), 6.63 (2H, s), 6.71-6.76 (2H, m), 7.02-7.09 (4H, m), 7.18 (2H, s), 7.24-7.28 (2H, m), 7.57-7.61 (2H, m), 8.09-8.13 (2H, m); HRMS calcd $C_{43}H_{34}N_2O_6$ 674.2417, found 674.2423. Anal. Calcd for: ($C_{43}H_{34}N_2O_6$ + 0.5H_2O): C, 75.53; H, 5.16; N, 4.10. Found: C, 75.29; H, 5.20; N, 4.05. **Adduct 4ba**: m p 318-319 °C; colorless prisms (ethanol); IR 2920, 1716, 1526, 1347, 1102, 756 cm^{-1}; ^1H NMR: 2.39 (2H, brs.), 2.73-2.83 (4H, m), 3.03 (2H, s), 3.35-3.46 (4H, m), 4.04 (4H, br. s), 4.41 (2H, s), 6.66-6.70 (2H, m), 6.75 (2H, s), 6.79 (2H, br. s), 6.96-6.98 (4H, m), 7.05-7.14 (4H, m), 8.08-8.11 (2H, m); HRMS calcd for $C_{43}H_{34}N_2O_6$ 674.2417, found 674.2422.

Adducts 3bb and 4bb. The general procedure was followed, reacting **1b** (10 mg, 0.02 mmol) and **2b** (5 mg, 0.02 mmol) for 20 h. HPLC of the residue with dichloromethane gave **3bb** (7 mg, 48%) and **4bb** (5 mg, 34%). **Adduct 3bb**: m p 350-351 °C; colorless prisms (ethanol); IR 3050, 2920, 1716, 1494, 1381, 1102, 754 cm^{-1}; ^1H NMR: 1.54 (2H, s), 2.42 (2H, brs.), 2.74-2.81 (2H, m), 2.93-3.01 (2H, m), 3.38-3.44 (2H, m), 3.59-3.64 (2H, m), 4.12 (4H, s), 4.22 (2H, s), 6.38-6.39 (2H, m), 6.62 (2H, s), 7.04-7.07 (4H, m), 7.16 (2H, s), 7.21-7.26 (4H, m), 7.55-7.60 (2H, m); HRMS Calcd for $C_{43}H_{34}ClNO_4$ 663.2176 and 665.2173, found 663.2173 (100.0) and 665.2145 (42.6). Anal. Calcd for ($C_{43}H_{34}ClNO_4$ + H_2O): C, 75.71; H, 5.31; N, 2.05. Found: C, 76.07; H, 5.25; N, 2.02. **Adduct 4bb**: m p 307-308 °C; colorless prisms (ethanol); IR 2960, 2924, 1717, 1493, 1385, 1261, 1098, 1037, 801 cm^{-1}; ^1H NMR: 2.37 (2H, brs.), 2.70-2.81 (4H, m), 3.01 (2H, s), 3.31-3.43 (4H, m), 4.02-4.03 (4H, m), 4.38 (2H, s), 6.25-6.28 (2H, m), 6.65 (2H, s), 6.80-6.85 (2H, m), 6.96 (2H, s), 7.08-7.13(6H, m), 7.23-7.26 (2H, m); HRMS calcd for $C_{43}H_{34}ClNO_4$ 663.2176 and 665.2173, found: 663.2187 (38.9) and 665.2115 (19.4).

Adducts 3bc, 4bc, and 5bc. The general procedure was followed, reacting **1b** (10 mg, 0.02 mmol) and **2c** (5 mg, 0.02 mmol) for 20h. HPLC of the residue with dichloromethane gave **3bc** (5 mg, 34%) and a mixture of **4bc** and **5bc** (7 mg, 48%). **Adduct 3bc**: mp 330-331 °C; colorless prisms (ethanol): IR 2920, 1714, 1513, 1255, 1094, 1034, 751 cm^{-1}; ^1H NMR: 1.66 (2H, s), 2.40 (2H, brs.), 2.71-2.79 (2H, m), 2.93-2.99 (2H, m), 3.39-3.45(2H, m), 3.59-3.64 (2H, m), 3.75 (3H, s), 4.12 (4H, s), 4.22 (2H, s), 6.27-6.30 (2H, m), 6.62 (2H, s), 6.78-6.79 (2H, m),7.05 (4H, s), 7.16 (2H, s), 7.23-7.27 (2H, m), 7.55-7.60 (2H, m); HRMS calcd for $C_{44}H_{37}NO_5$ 659.2672, found 659.2674. Anal. Calcd for : ($C_{44}H_{37}NO_5$ + 0.5H_2O): C, 79.02; H,

Table 2. Crystallographic Data Collections and Refinements.

Compound	**4aa**
Formula	$C_{40}H_{34}Cl_2N_2O_6$
Formula Weight	709.59
Temperature	20 °C
Crystal System	monoclinic
Space Group	$P2_1/n$
Unit Cell Dimensions	
a	10.395 (2)
b	33.875 (2)
c	9.571 (8)
α	90.00
β	96.07
γ	90.00
Volume	3351.46
Z	4
Density (Calculated)	1.41
Crystal Size (mm)	0.27 * 0.23 * 0.20
q range	2.61-89.20
Index ranges	
h	0-11
k	0-39
l	-12-12
Radiation	CuKα
Monochromater	Graphite Crystal, Incident Beam
Data Collection Mode	ω–2θ scan
No. Refl. Measd.	6194
No. Unique Refl.	6194
No. Refl. $F > 3\sigma$ (F)	3874
Lin. Abs. Coeff. (mm^{-1})	0.64
Data/Parameter Ratio	11.80
R, *Rw*	0.0675, 0.1973
Weighting Scheme	$w= 1/[\sigma^2(Fo^2)+0.1508P)^2+1.0397P]$, where $P= (Fo+2Fc^2)/3$
Largest Diff. Peak/Hole (e. A^{-3})	0.33/-0.35
Solution by	Direct Method SIR 92
Method of Refinement	Full Matrix LSQ for F^2, hydrogen positions of riding model with fixed isotropic U, U=1.3 times U of the riding atoms.
Diffractometer	Enraf-Nonius FR-590
Program Used	Shelxl 93

5.73; N, 2.09. Found: C, 78.99; H, 5.76; N, 2.05. **Mixture of 4bc and 5bc**: mp 300-302 °C; colorless prisms (ethanol): IR 2960, 2924, 1715, 1512, 1390, 1260, 1093, 1029, 802 cm^{-1}; HRMS calcd for $C_{44}H_{37}NO_5$ 659.2672, found 659.2660. ^1H NMR of **4bc**: 2.38 (2H, br. s), 2.68-2.80 (4H, m), 2.98 (2H, s), 3.28-3.32 (4H, m), 3.75 (3H, s), 3.98-4.03 (4H, m), 4.38 (2H, s), 6.17-6.20 (2H, m), 6.63 (2H, s), 6.73-6.79 (2H, m), 6.80-6.85 (2H, m), 6.97 (2H, s), 7.10-7.15(6H, m). ^1H NMR of **5bc**: 2.38 (2H, br. s), 2.68-2.80 (4H, m), 2.95 (2H, s), 3.28-3.32 (4H, m), 3.73 (3H, s), 3.98-4.03 (4H, m), 4.38 (2H, s), 6.23-6.27 (2H, m), 6.73-6.79 (2H, m), 6.80-6.85 (2H, m), 6.97 (2H, s), 6.98 (2H, s), 7.10-7.15(6H, m).

Single crystal X-ray diffraction analysis of 4aa. The crystallographic measurement was carried out at 296 K on an Enraf-Nonius FR-590 diffractometer operating in the $\omega-2\theta$ scan mode using graphite monochromated CuKα-radiation (λ= 1.54184 Å). The structure of **4aa** was solved by direct method using SIR 92[11] and refined by full-matrix least-squares using Shelxl. Refinement was essentially that all-non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were constrained to calculated positions. The weighting scheme $w = 1/[\sigma^2(Fo^2)+0.1508P)^2+1.0397P]$, where $P= (Fo+2Fc^2)/3$, was used. Crystallographic data collections and method of refinements are given in **Table 2**. The supplementary materials have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgment. We are grateful to Dr. Nobuo Kato of the Institute of Advanced Material Study, Kyushu University for valuable discussions and measurements of NOE spectra.

References

1 1a) Mataka, S.; Ma, J.; Thiemann, T.; Rudzinski, J. M.; Sawada, T.; Tashiro, M. *Tetrahedron Lett.*, **1995**, *34*, 6105-6108. 1b) Mataka, S.; Ma, J.; Thiemann, T.; Rudzinski, J. M.; Tsuzuki, H.; Sawada, T.; Tashiro, M. *Tetrahedron* , **1997**, *53*, 885-902.

2 Hesse, M.; Meier, H.; Zeeh, B. " Spektroskopische Methoden in der Organischen Chemie", Thieme Verlag, Stuttgart, 151 (1979).

3 Kobuke, Y.; Fueno, T.; Furukawa, J. *J. Am. Chem. Soc.* **1970**, *92*, 6548-6553.

4 Pawliszyn, J.; Szczesniak, M. M.; Scheiner, S. *J. Phys. Chem.*, **1984**, *88*, 1726-1730.

5 Burley, S. K.; Petsko, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 7995-8001.

6 Price, S. L.; Stone, A. J. *J. Chem. Phys.*, **1987**, *86*, 2859-2868.

7 Jorgensen, W. L.; Seyerance, D. L. *J. Am. Chem. Soc.*, **1990**, *112*, 4768-4774.

8 Nishio, M.; Hirota, M. *Tetrahedron* **1989**, *45*, 7201-7245.

9 9a) Hunter, C. A.; Sanders, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525-5534. 9b) Hunter, C. A. *J. Chem. Soc., Chem. Commun.* **1991**, 749-751. 9c) Hunter, C. A. *Chem. Soc. Rev.* **1994**, 101-109.

10 Paliwal, S.; Geib, S.; Wilcox, C. S. *J. Am. Chem. Soc.* **1994**, *116*, 4497-4498.

11 Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343-350.

(*Received in Japan* 20 *February* 1997; *accepted* 24 *March* 1997)