Benzo[*b*]cyclohept[*e*][1,4]oxazines§ IV.[1] Synthesis and Properties of All Possible Benzoxazinotropones[2]

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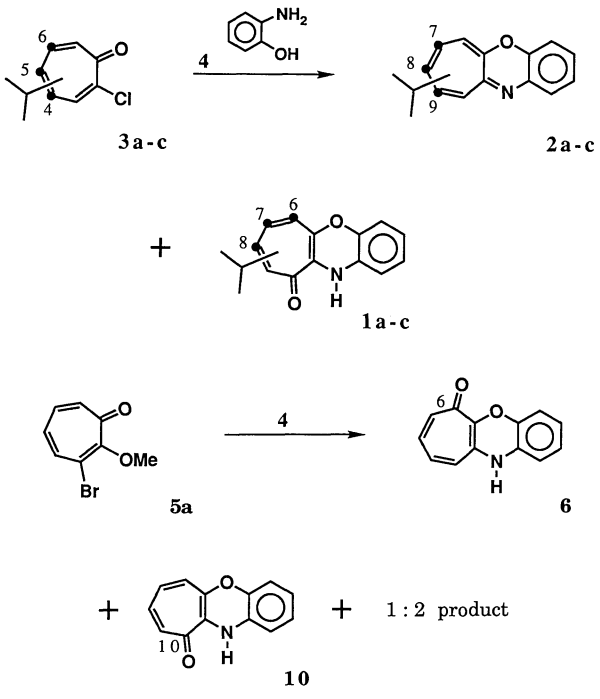
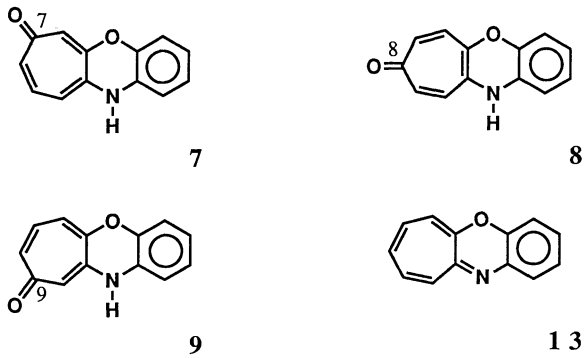
Five isomeric benzo[*b*]cyclohept[*e*][1,4]oxazin-6~10-ones (hereafter refered to as benzoxazinotropones) and bromobenzoxazinotropones were prepared almost quantitatively by the hydrolysis of the corresponding mono-, di-, and tribromobenzo[*b*]cyclohept[*e*][1,4]oxazines with refluxing acetic acid. On the basis of spectral data and theoretical calculations, benzo[*b*]cyclohept[*e*][1,4]oxazin-6~9(11*H*)-ones are believed to exist in the keto form. These compounds gave respective methoxy- and acetoxybenzo[*b*]cyclohept[*e*][1,4]oxazines when reacted with diazomethane and acetic anhydride. On the other hand, benzo[*b*]cyclohept[*e*][1,4]oxazin-10(11*H*)-one was found to exist in a stable, intermolecularly hydrogen-bonded form and did not form acetoxylated or methylated compounds. Possible reaction pathways for the formation of these products are discussed.

One of the authors (T.N.) and his co-worker reported[3] that a small amount (less than 1%) of isomeric isopropylbenzo[*b*]cyclohept[*e*][1,4]oxazin-10(11*H*)-ones (**1a—c**) were produced along with the main products 7-, 8-, and 9-isopropylbenzo[*b*]cyclohept[*e*][1,4]oxazines (**2a—c**), when isomeric 2-chloro-4-, 5-, and 6-isopropyltropones (**3a—c**) were refluxed in acetic acid with *o*-aminophenol (**4**). We later reported[4] that the condensation of 3-bromo-2-methoxytropone (**5a**) with an excess of **4** in refluxing acetic acid gave a small amount of benzo[*b*]cyclohept[*e*][1,4]oxazin-6(11*H*)-one (**6**), and its 10(11*H*)-one isomer (**10**) as 1:1-condensation products, along with various interesting 1:2-condensation products. Although some possible reaction pathways for the formation of **6** and **10** (and for **1**) were presented, we did not have enough experimental evidence to distinguish between them.[1] In this paper we wish to describe the details of the synthesis, structures, and keto-enol tautomerism of all possible isomers of the benzo[*b*]cyclohept[*e*][1,4]oxazin-6~10(11*H*)-ones (hereafter refered to as benzoxazinotropones, **6—10**), as well as a possible mechanism for the formation of these compounds.





Results and Discussion

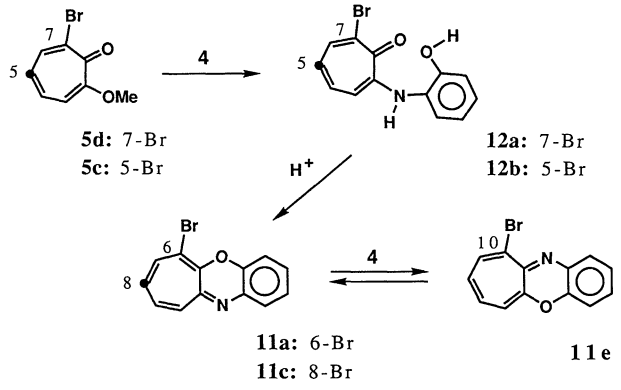
Synthesis of Various Bromobenzo[*b*]cyclohept[*e*]-[1,4]oxazines (11a—e). 6-Bromo- (**11a**)[5] and 8-bromobenzo[*b*]cyclohept[*e*][1,4]oxazine (**11c**)[6] were respectively prepared by the condensation of 7-bromo- (**5d**) and 5-bromo-2-methoxytropone (**5c**) with **4**, via the respective bromo-2-(2-hydroxyanilino)tropones (**12a, b**). The 10-bromo compound (**11e**) was obtained from **11a** by an intermolecular heterocycle exchange reaction[7] with **4** in

§ Benzo[*b*]cyclohept[*e*][1,4]oxazine was refered to as cyclohepta[*b*][1,4]benzoxazine in the preceding paper.

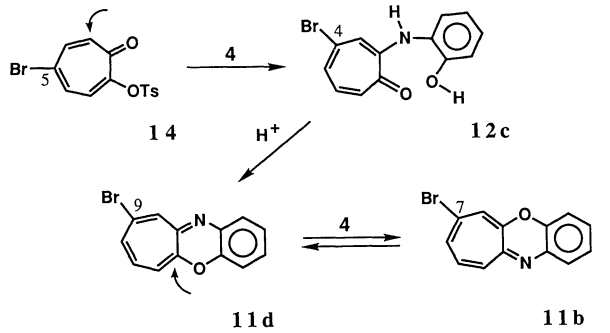
methanol (Scheme 1).

The reaction of 5-bromotropolone *p*-toluenesulfonate (**14**) with **4** in pyridine gave anilinotropone **12c** (84% yield) through cine substitution.[8] Compound **12c** underwent cyclization in hot acetic acid containing a trace amount of concd sulfuric acid to give **11d** (82% yield, Scheme 2). The structures of **12c** and **11d** were determined to be 4-bromo-2-(2-hydroxyanilino)tropone and 9-bromobenzo[*b*]cyclohept[*e*][1,4]oxazine, respectively, on the basis of the spectral data (see the Experimental section).

The reaction of **11d** with 2 equiv of **4** in MeOH at room temperature was studied by time-dependent HPLC. It



Scheme 1.



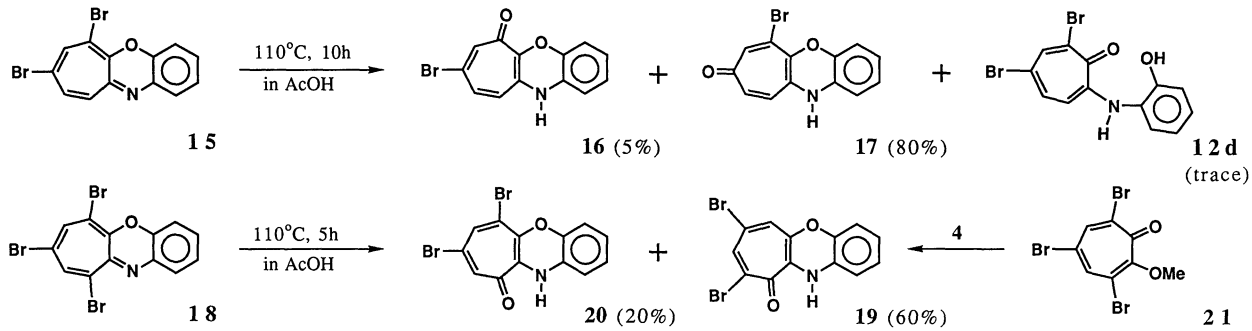
Scheme 2.

was determined that **11d** and **11b** attained an approximately 1:1 equilibrium within 1 h by an intermolecular heterocycle exchange reaction (Scheme 2).[7] The reaction mixture was separated by silica-gel chromatography and **11b** (45% yield) was identified as 7-bromobenzo[*b*]cyclohept[*e*][1,4]oxazine on the basis of NMR spectra and comparison of its UV spectra with **11d**.

Synthesis of Benzoxazinotropones. Heating of bromo compounds **11a—e** in acetic acid at 110 °C for 20 min to 2 h (depending on the position of the Br atom) gave the corresponding benzoxazinotropones (**6—10**) in nearly quantitative yields. Compounds **6** and **10** were identified as benzo[*b*]cyclohept[*e*][1,4]oxazin-6(11*H*)-one and -10(11*H*)-one, respectively, by direct comparison with the authentic samples.[4] The structure of **7** was shown spectroscopically to be benzo[*b*]cyclohept[*e*]-[1,4]oxazin-7(11*H*)-one. Compounds **8** and **9** were also shown to be benzo[*b*]cyclohept[*e*][1,4]oxazin-8(11*H*)-one and -9(11*H*)-one, respectively, on the basis of the spectral data (see the Experimental section).

Similarly, 6,8-dibromobenzo[*b*]cyclohept[*e*][1,4]-oxazine (**15**)[6] produced two bromobenzoxazinotropones (**16** (5% yield) and **17** (80% yield)) as well as a small amount of **12d**. The structures of **16** and **17** were determined to be 8-bromobenzo[*b*]cyclohept[*e*][1,4]-oxazin-6-(11*H*)-one and 6-bromobenzo[*b*]cyclohept[*e*]-[1,4]oxazin-8(11*H*)-one, respectively, on the basis of high resolution mass spectral data and comparison of their UV spectra with those of **6** and **8**, as well as the results of acylation (see below). On the other hand, 6,8,10-tribromobenzo[*b*]cyclohept[*e*][1,4]oxazine (**18**)[9] gave, under similar conditions, isomeric dibromobenzoxazinotropones **19** (60% yield) and **20** (20% yield). Zinc dust reduction of compounds **19** and **20** resulted in the same benzoxazinotropone **10**. Compound **19** was also prepared by the reaction of 2,4,6-tribromo-7-methoxytropone (**21**) with **4**. This evidence along with the spectral data mentioned above showed the structures of **19** and **20** to be 7,9-dibromo- and 6,8-dibromobenzo-[*b*]cyclohept[*e*][1,4]oxazin-10(11*H*)-one, respectively (Scheme 3).

Hydrolysis of **18** with AcOH gave only the dibromo derivatives of benzo[*b*]cyclohept[*e*][1,4]oxazin-10(11*H*)-one (**10**), but neither 6(11*H*)-one nor 8(11*H*)-one deriva-



Scheme 3.

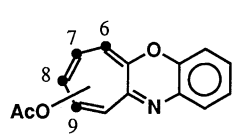
tives were produced, whereas the same treatment of **15** gave a mixture of 6(11*H*)-one derivative **16** and 8(11*H*)-one derivative **17** in a 1:16 ratio. These results suggest that the facility of the hydrolytic cleavage is in order C-10>C-8>C-6.

The bonding energies between the Br-attached carbon and Br of **11a—e** were calculated by the MINDO/3 method to be −11.38, −11.27, −11.32, −11.31, and −11.34 eV, respectively. In the case of **15**, the binding energy between C-6 and Br was calculated to be −11.45 eV, while that between C-8 and Br was −11.35 eV. Therefore, the bond between C-8 and its Br atom is hydrolyzed more readily than the bond between C-6 and its Br atom. In the case of **18**, the binding energies between a Br-attached carbon and its Br atom are in order C-6 (−11.47 eV) < C-8 (−11.42 eV) < C-10 (−11.40 eV). These results agree with the order of the facility of the hydrolytic cleavage.

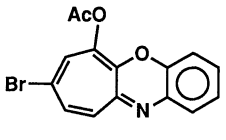
Keto-Enol Tautomerism of Benzoxazinotropones. Keto-enol tautomerism is believed to exist in compounds **6—10**. In order to clarify the tautomerism, the acetylation and methylation of benzoxazinotropones **6—10** were studied. Moreover, HMO[10] and MINDO/3[11] molecular orbital theoretical calculations were performed and the theoretical results were compared with the experimental results.

6-10 **6a-10a**

a) Acylation and Methylation. No products were obtained when **6—10** were combined with acetic anhydride in pyridine at 80 °C. However, acetates **22a—d** were produced in ca. 80% yields when **6—9** were mixed with acetic anhydride in acetic acid containing a trace amount of concd sulfuric acid at room temperature. Compound **22a** was determined to be 6-acetoxybenzo[*b*]cyclohept[*e*][1,4]oxazine from the high resolution mass spectral determination of molecular weight (*m*/*z* M^+, 253.0769) and other spectral data. The IR spectrum showed an *O*-acetyl carbonyl absorption peak near 1770 cm^{-1}. The electronic spectrum is very similar to that of the parent compound **13**. The structures of **22b—d** were also identified as 7-, 8-, and 9-acetoxybenzo[*b*]cyclohept[*e*][1,4]oxazine, respectively, on the basis of their NMR and other spectral data (see the Experimental section). Similarly, **16** and **17** were reacted as above to form acetoxyl derivatives **23** and **24**, respectively. Acetylated compounds **22a—d**, **23**, and **24** reverted to the corresponding benzoxazinotropones **6—9**, **16**, and **17** when treated with refluxing acetic acid for about 5 min.



22a-d



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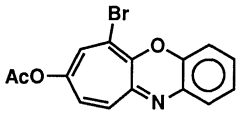

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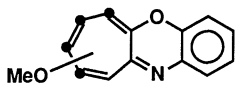


25a-d

Compounds **6—9** reacted slowly with diazomethane to give the corresponding methylated products **25a—d** as brown needles. However, **10** did not result in acetylated and methylated compounds under similar conditions. The structures of **25a—d** were assigned to 6-, 7-, 8-, and 9-methoxybenzo[*b*]cyclohept[*e*][1,4]oxazines, respectively, on the basis of their NMR and other spectral data (see the Experimental section). Methylated compounds **25a—d** gradually reverted to the corresponding benzoxazinotropones **6—9** on standing in methanol at room temperature.

b) Theoretical Calculations. The resonance energies and bond currents of the keto forms **6—10** and the enol forms **6a—10a** have been calculated by means of Aihara's graph theory of aromaticity.[12] The HMO theory is assumed to be in its simplest form. Streitwieser[10] evaluated the heteroatom parameters for the amine nitrogen, the

Table 1. Resonance Energies, Heats of Formation, and Circuit Resonance Energies for Keto Forms (**6—10**) and Enol Forms (**6a—10a**)

Compd	RE	ΔH_f	CRE		Compd	RE	ΔH_f	CRE	
		kcal mol^{-1}	r_1	r_3			kcal mol^{-1}	r_1	r_3
6	0.401	−25.1	0.152	0.216	**6a**	0.312	−22.2	0.126	0.201
7	0.404	−35.4	0.142	0.213	**7a**	0.319	−31.8	0.117	0.197
8	0.402	−29.1	0.151	0.216	**8a**	0.314	−28.4	0.125	0.200
9	0.403	−35.0	0.142	0.213	**9a**	0.318	−30.7	0.117	0.197
10	0.402	−30.0	0.152	0.216	**10a**	0.315	−27.2	0.130	0.201

RE: Resonance energy (in β units). CRE: Circuit resonance energy (in β units). ΔH_f: Heats of formation calculated by the MINDO/3 method.

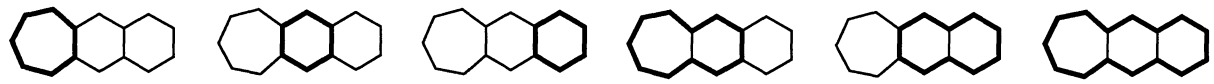
imine nitrogen, the ether oxygen, and the ketone oxygen. We have used these values in this paper.

MINDO/3[11] is a reasonably reliable method for the prediction of heats of formation. The molecular geometries of **6**—**10** and its enol forms **6a**—**10a** were calculated by MINDO/3 optimizations. In all cases, the MINDO/3 optimized geometries were planar and exhibited appreciable bond alternation. As shown in Table 1, the heats of formation of the keto forms are more stable than those of the enol forms by 0.7—4.3 kcal mol^{-1}.

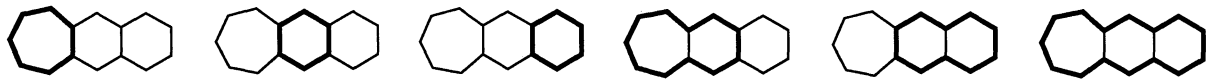
All the keto and enol compounds are predicted to be aromatic with positive resonance energies.[12a] The keto form species have larger resonance energies than those of the enol forms. With a view to clarifying the origin of the aromaticity, we calculated the circuit resonance energies[12c] of the keto forms by means of Aihara's graph theory of aromaticity. The π-electron ring system in the keto forms consists of six π-ring components, from r_1 to r_6, as shown in Fig. 1. Geometrically unidentical π-electron circuits are shown and numbered in Fig. 1. The results are listed in Table 1. The circuit resonance energies of r_1 and r_3 are positive, while those of r_2, r_4, r_5, and r_6 are near zero or negative. Consequently, the keto form compounds are stabilized as the 6-π-tropylium-6-π-benzenoid form.

Since **6**—**10** are only slightly soluble in less polar solvents, the NMR spectra were measured in DMSO-d_6. In all cases, the ^{13}C NMR spectra exhibited a peak at about δ=180 resulting from a carbonyl group. These results match the keto form but not the enol form in a polar solvent such as DMSO. In the ^1H NMR spectra, the chemical shifts of the seven-membered ring protons for **6**—**10** differ from those of parent compound **13**. This can also be explained by assuming the compounds are in the keto form. This causes the signals of the β proton of the carbonyl groups to appear at a lower field compared with those of compounds **13**, **22**, and **25**. The observed values of the average chemical shifts of the seven-membered ring protons and benzene ring protons of **6**—**10** are at δ=6.61 and 6.70, respectively. In contrast, the chemical shifts of the seven-membered ring protons of the enol forms and **13** are expected to be much higher than those of the benzene ring protons.[13] Furthermore, ring currents of the keto forms of **6**—**10** and their enol forms **6a**—**10a** have been calculated by Aihara's method,[12b] and the results are shown in Fig. 1. The average ring currents of the seven-membered rings (r_1) and benzene rings (r_3) of **6**—**10** are 0.930 I_0 and 1.000 I_0, respectively, whereas those of **6a**—**10a** are 0.710 I_0 and 1.040 I_0 respectively. We therefore conclude that benzoxazinotropones **6**—**10** exist mainly in the keto form on the basis of the experimental facts, NMR spectral data, and theoretical calculations.

Though compounds **6**—**9** were almost the same yellow-brown color and had very similar electronic absorption bands, **10** had a red color. The electronic spectra of **10**, in methanol solution, showed the longest



	r_1	r_2	r_3	r_4	r_5	r_6
6	0.956 I_0	-0.026 I_0	0.974 I_0	-0.064 I_0	-0.044 I_0	0.064 I_0
7	0.895 I_0	-0.001 I_0	0.956 I_0	-0.061 I_0	-0.005 I_0	0.060 I_0
8	0.952 I_0	-0.023 I_0	0.973 I_0	-0.064 I_0	-0.041 I_0	0.063 I_0
9	0.895 I_0	-0.001 I_0	0.957 I_0	-0.061 I_0	-0.005 I_0	0.060 I_0
10	0.957 I_0	-0.026 I_0	0.973 I_0	-0.064 I_0	-0.043 I_0	0.063 I_0



	r_1	r_2	r_3	r_4	r_5	r_6
6a	0.792 I_0	0.045 I_0	0.904 I_0	-0.194 I_0	0.004 I_0	0.107 I_0
7a	0.734 I_0	0.066 I_0	0.885 I_0	-0.182 I_0	0.043 I_0	0.100 I_0
8a	0.788 I_0	0.031 I_0	0.902 I_0	-0.192 I_0	0.007 I_0	0.106 I_0
9a	0.734 I_0	0.051 I_0	0.887 I_0	-0.184 I_0	0.042 I_0	0.101 I_0
10a	0.818 I_0	0.007 I_0	0.904 I_0	-0.146 I_0	0.040 I_0	0.169 I_0

Fig. 1. Ring currents of **6**—**10** and **6a**—**10a**. (I_0=Ring currents of benzene).

wavelength band centered at 480 nm. We have also calculated the electronic transitions for **6**—**10** by the CNDO/S-CI method. For example, the spectra of **7** showed an absorption band, deriving from the HOMO–LUMO transition, lying in the UV region at 3.13 eV (395 nm). The electronic transitions calculated by adopting the MINDO/3 geometries of **10** are predicted to have $\pi\pi^*$ λ_{max} of 2.73 eV (454 nm, f=0.000), 2.75 eV (450 nm, f=0.000), 2.98 eV (416 nm, f=0.094), and 3.05 eV (406 nm, f=0.072) in the long wavelength region. The calculated results, however, do not conform to the electronic spectra of **10**.

To elucidate the molecular structure of **10**, an X-ray diffraction analysis was carried out.[14] The molecular framework is illustrated in Fig. 2. The definitive structure determination of **10** was particularly interesting, because this compound was shown to exist in an intermolecularly hydrogen-bonded form in the solid state.

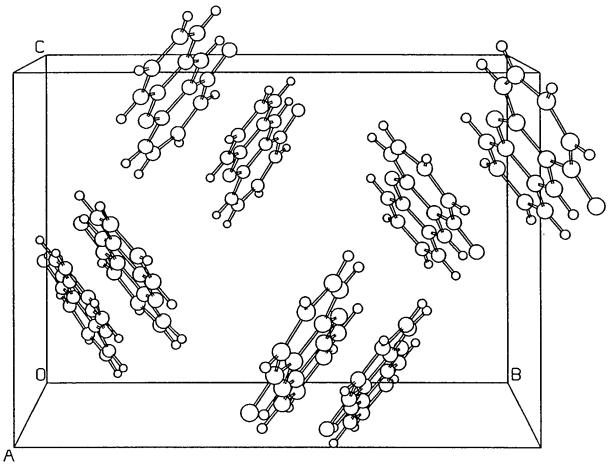


Fig. 2. A perspective view of **10**.

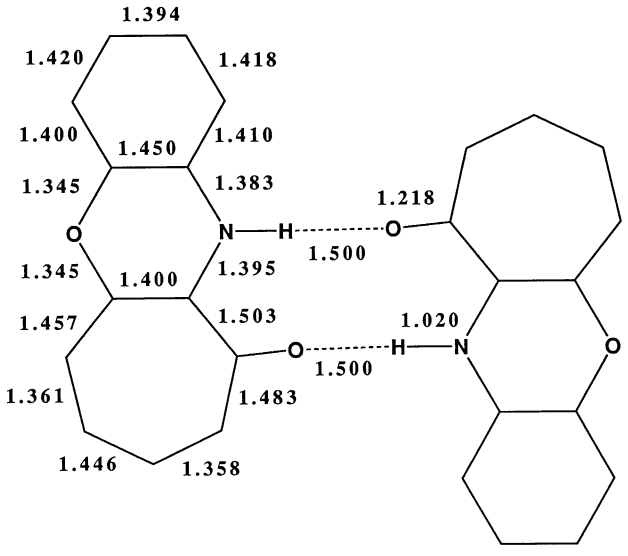


Fig. 3. Assumed structure of Model A. Bond lengths are expressed in Angstroms (Å).

The *H*-bond is between the ketone oxygen in one molecule and the imine hydrogen in another molecule. We therefore propose two dimeric model structures on the basis of the above X-ray experimental geometry and MINDO/3 optimized values. Model A is a planar molecule with an assumed N···O bond length of 2.718 Å (Fig. 3), whereas Model B is a nonplanar molecule. The geometries of Model B are the same as those of Model A, except that the separation of two molecular planes is assumed to be 1.9 Å and the N···O bond length is 2.2 Å. The calculated electronic transitions of Model A are predicted to have $\pi\pi^*$ λ_{max} of 2.57 eV (481 nm, f=0.000), 2.80 eV (442 nm, f=0.000), 2.85 eV (435 nm, f=0.166), and 2.96 eV (418 nm, f=0.238) in the long wavelength region and are very close to the calculated transitions of monomeric compound **10**. The calculated electronic transitions of Model B are predicted to have $\pi\pi^*$ λ_{max} of 2.48 eV (500 nm, f=0.002), 2.53 eV (490 nm, f=0.215), 2.84 eV (436 nm, f=0.012), 2.92 eV (424 nm, f=0.151), 2.93 eV (423 nm, f=0.180), and 3.06 eV (405 nm, f=0.051) in the same region. In the calculated results of Model B, its next longest absorption band can be attributed to an intermolecular charge-transfer transition from one molecule to another molecule because this absorption band was assigned to a HOMO–LUMO transition, and π charges in HOMO or LUMO orbitals were distributed on each molecule of the assumed dimer. The electronic transitions calculated for Model B agree with the expeprimental electronic spectra of **10**. The agreement between calculated and experimental data is satisfactory, especially if we bear in mind that theoretical values refer to the gas phase and experimental values to the solution state.

Possible Reaction Pathways for the Formation of Benzoxazinotropones. As mentioned above, bromo compounds **11a**—**e** gave an almost quantitative yield of benzoxazinotropones **6**—**10**, respectively, upon heating in 97% acetic acid. However, upon heating in ethanol, **11a**—**d** did not result in benzoxazinotropones **6**—**9**, while **11e** gave **10** almost quantitatively. Additionally, by periodically checking the reaction with reversed-phase HPLC we observed the formation of **22d** when **11d** was heated in anhydrous acetic acid at 110 °C. As shown in Fig. 4, a peak corresponding to acetoxyl compound **22d** appears first, then the peak corresponding to **9** increases as the peaks corresponding to **22d** and **11d** decrease in the chromatogram. In this transformation, as shown in Scheme 4, intermediate **a** may be produced first by the attack of an acetoxyl anion (not by moisture in the acetic acid) at the bromine-substituted C-9 position of **11d**. Compound **a** may then give **9** via acetoxyl derivative **22d**. Similarly, **11a**—**c** are likely to produce **6**—**8** via acetoxyl compounds **22a**—**c**, respectively, and **15** is likely to produce **16** and **17** via acetoxyl compounds **23** and **24**, respectively.

As we reported earlier,[7] position C-5a in the benzo[*b*]cyclohept[*e*][1,4]oxazine nucleus is most easily

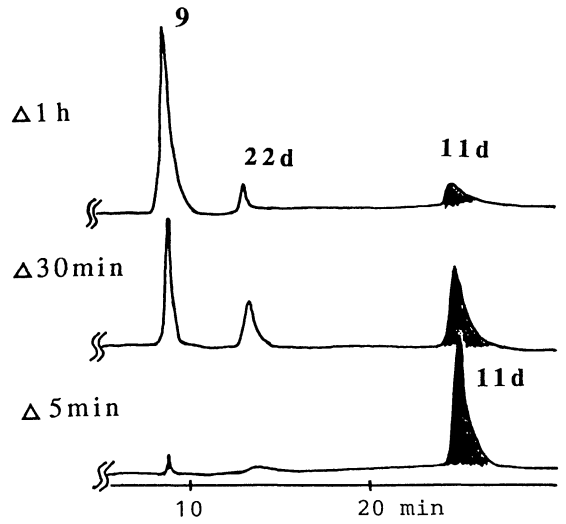
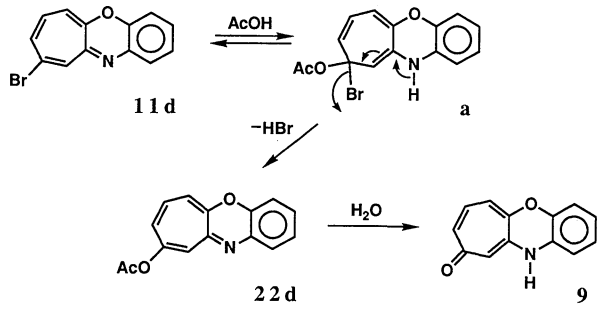
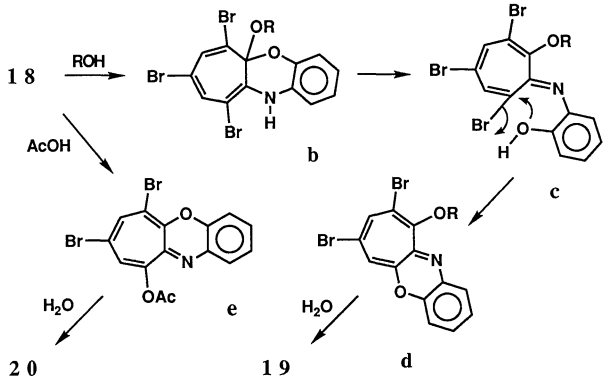


Fig. 4. Time-dependent HPLC chromatograms of the hydrolysis of **11d** in dry AcOH at 110°C.



Scheme 4.



Scheme 5.

attacked by nucleophiles, and when the C-10 position is substituted with a group such as a bromine atom, that group acts as a good leaving group. Therefore, it is quite understandable that the 10-bromo compound **11e** is readily transformed to **10** even in MeOH (containing a small amount of water), and the tribromo compound **18** gives 7,9-dibromobenzoxazinotropone **19** as the main product along with the 6,8-dibromo compound **20**, as illustrated in Scheme 5.

Experimental

Melting points were determined with a Yanagimoto MP-3S melting point apparatus and were uncorrected. The IR and electronic spectra were measured by using a Shimadzu IR-450 and a Shimadzu UV-265FS spectrometer, respepctively; the UV spectra in acid and alkali solutions were taken after adding a few drops of 6 M HCl or 6 M NaOH (1 M=1 mol dm^{-3}) to the sample solution. The NMR spectra were measured in $CDCl_3$ (unless otherwise specified) with a JEOL JNM-PS/PET (100 MHz) or a JEOL JNM-GX270 (270 MHz for 1H and 67.8 MHz for ^{13}C) spectrometer using TMS as the internal standard. The assignments of all signals were made by employing a first-order analysis with the aid of a decoupling technique. The mass spectra were taken on a JEOL JMS-DX300 mass spectrometer and a Shimadzu LKB 9000 GC-mass spectrometer at 70 eV. The HPLC was carried out on Hitachi gel #3011 with MeOH–hexane (9:1) as the solvent. The centrifugal chromatography was performed with a Hitachi CLC-5 instrument in a Fuji silica-gel layer (KT-2151, 3 mm thickness) using benzene as an eluent. The TLC analyses were carried out with Merck Kieselgel 60F-254 plates.

4-Bromo-2-(2-hydroxyanilino)tropone (12c). A mixture of 5-bromotropolone *p*-toluenesulfonate[15] (**14**, 506 mg, 1.42 mmol) and *o*-aminophenol (**4**, 310 mg, 2.82 mmol) in pyridine (5 cm^3) was heated at 60°C for 5 h. The solvent was evaporated in vacuo and the residue was chromatographed on a column of silica gel with benzene–MeOH (50:1), giving **12c** (345 mg, 84% yield):Orange needles (from MeOH); mp 170—172°C (decomp); UV_{max} (MeOH) 240 (log ε 4.20), 262 (4.31), 347 (4.04), and 407 nm (4.18), (MeOH+ 6 M NaOH) 244 (log ε 4.29), 272 (4.17), 346 (3.89), and 413 nm (4.11); IR (KBr) 3430 (OH) and 3250 cm^{-1} (NH); ^1H NMR (270 MHz, CD_3OD) δ=6.96 (1H, td, *J*=8.0 and 2.0 Hz, H-5′), 7.00 (1H, dd, *J*=8.0 and 2.0 Hz, H-3′), 7.05—7.10 (4H, m, H-3,5,6,7), 7.20 (1H, td, *J*=8.0 and 2.0 Hz, H-4′), and 7.28 (1H, dd, *J*=8.0 and 2.0 Hz, H-6′). Found: C, 53.26; H, 3.57; N, 4.60%; M^+, 292. Calcd for $C_{13}H_{10}NO_2Br$: C, 53.45; H, 3.45; N, 4.79%; M, 292.

9-Bromobenzo[*b*]cyclohept[*e*][1,4]oxazine (11d). A solution of **12c** (210 mg) in acetic acid (5 cm^3) containing a trace amount of concd sulfuric acid was heated at 120°C for 2 h under nitrogen. The solvent was then evaporated in vacuo. The residue was neutralized with aq $NaHCO_3$ and extracted twice with benzene. The extracts were combined, dried (Na_2SO_4) and evaporated in vacuo. The residue was chromatographed centrifugally on a layer of silica gel with benzene as the eluent, giving **11d** (161 mg, 82% yield): Brown needles; mp 145—147°C (from benzene); UV_{max} (MeOH) 263 (log ε 4.47), 270 (4.47), 305 (4.03), and 414 nm (4.10), (MeOH +6M HCl) 267 (log ε 4.37), 287 (4.27), 320 (4.15), and 449 nm (3.99); ^1H-NMR (270 MHz) δ=5.29 (1H, d, *J*=9.8 Hz, H-6), 5.70 (1H, dd, *J*=11.5 and 9.8 Hz, H-7), 5.90 (1H, dd, *J*=11.5 and 2.0 Hz, H-8), 6.40 (1H, m, H-4), 6.54 (1H, d, *J*=2.0 Hz, H-10), and 6.78 (3H, m, H-1,2,3). Found: C, 57.00; H, 3.08; N, 4.99%; M^+, 274. Calcd for $C_{13}H_8NOBr$: C, 56.96; H, 2.94; N, 5.11%; M, 274.

7-Bromobenzo[*b*]cyclohept[*e*][1,4]oxazine (11b). A mixture of **11d** (30 mg, 0.11 mmol) and **4** (24 mg, 0.22 mmol) in methanol (5 cm^3) was allowed to stand for 1 h at room

temperature. The reaction contents were checked by means of time-dependent HPLC. The solvent was evaporated in vacuo. The residue was chromatographed on silica-gel thin-layer plates with benzene as the eluent. The product was recrystallized from benzene, giving **11b** (13 mg, 45% yield)(along with 50% recovered **11d**): Brown needles; mp 130—132 °C; UV_{max} (MeOH) 222 (log ε 4.31), 262 (4.39), 272 (4.36), 309 (4.15 sh), 322 (3.76 sh), and 415 nm (4.05), (MeOH+6 M HCl) 230 (log ε 4.35), 267 (4.30), 285 (4.17 sh), 317 (4.01), 439 (3.98), and 427 nm (3.87 sh); ^{1}H NMR (270 MHz) δ=5.69 (1H, d, *J*=1.5 Hz, H-6), 5.82 (1H, dd, *J*=12.4 and 8.8 Hz, H-9), 6.00 (1H, d, *J*=12.4 Hz, H-10), 6.12 (1H, dd, *J*=8.8 and 1.5 Hz, H-8), 6.43 (1H, m, H-4), and 6.73—6.85 (3H, m, H-1,2,3). Found: C, 56.74; H, 3.05; N, 4.89%; M$^+$, 274. Calcd for $C_{13}H_8NOBr$: C, 56.96; H, 2.94; N, 5.11%; M, 274.

Similarly, when a methanolic solution of **11b** and **4** was allowed to stand at room temperature, an additional peak due to compound **11d** began to appear in the HPLC chromatogram and an equilibrium was reached within a few hours. The isomerized **11d** was isolated in pure crystalline form.

Hydrolysis of 11a—e. A solution of **11c** (55 mg) in acetic acid (10 cm^3) was heated at 110 °C for 1 h, followed by the same procedures as those described above for **12c**. The residual solid was recrystallized from MeOH to give **8** (40 mg, 95% yield). Similarly, **6**[4] (95% yield), **7** (95% yield), **9** (90% yield), and **10**[4] (95% yield) were obtained from **11a, 11b, 11d,** and **11e**, respectively.

Benzo[*b*]cyclohept[*e*][1,4]oxazin-6(11*H*)-one (6): Mp 270—271 °C (lit,[4] mp 270 °C); UV_{max} (DMSO) 264, 305, 315, 330 (sh), and 393 nm, ($CHCl_3$) 259, 300, 310, 326 (sh), and 388 nm; ^{1}H NMR (270 MHz, DMSO-*d*$_6$) δ=6.42 (1H, dd, *J*=8.0 and 1.8 Hz, H-4), 6.49 (1H, dd, *J*=12.2 and 2.6 Hz, H-7), 6.56 (1H, dd, *J*=8.0 and 1.8 Hz, H-1), 6.64 (1H, td, *J*=8.0 and 1.8 Hz, H-2), 6.72 (1H, td, *J*=8.0 and 1.8 Hz, H-3), 6.81 (3H, m, H-8,9,10), and 8.57 (1H, br, NH); ^{13}C NMR (67.8 MHz, DMSO-*d*$_6$) δ=113.4 (d), 114.9 (d), 123.1 (d), 124.6 (d), 126.9 (d), 130.9 (s), 131.0 (d), 131.6 (d), 139.9 (s), 140.9 (d), 143.2 (s), 145.2 (s), and 173.3 (s).

Benzo[*b*]cyclohept[*e*][1,4]oxazin-7(11*H*)-one (7): Orange needles; mp 294—296 °C (from MeOH); UV_{max} (MeOH) 221 (log ε 4.27), 237 (4.14), 295 (4.29), 325 (3.70 sh), and 427 nm (4.02), (MeOH+6 M HCl) 225 (log ε 4.30), 256 (4.14), 287 (4.20), 309 (3.99 sh), and 452 nm (3.91),(MeOH+6 M NaOH) 258 (log ε 4.28), 300 (4.25), 465 (4.17), and 497 nm (4.08), (DMSO) 265, 289, 396 (sh), and 423 nm, ($CHCl_3$) 242, 288, 296, 390 (sh), and 413 nm; IR (KBr) 3250 and 1640 cm^{-1}; ^{1}H NMR (270 MHz, DMSO-*d*$_6$) δ=5.99 (1H, d, *J*=9.7 Hz, H-10), 6.13 (1H, dd, *J*=11.8 and 2.7 Hz, H-8), 6.33 (1H, d, *J*=2.7 Hz, H-6), 6.70 (1H, dd, *J*=8.0 and 1.8 Hz, H-4), 6.75 (1H, td, *J*=8.0 and 1.8 Hz, H-2), 6.81 (1H, dd, *J*=11.8 and 9.7 Hz, H-9), 6.84 (1H, dd, *J*=8.0 and 1.8 Hz, H-1), 6.89 (1H, td, *J*=8.0 and 1.8 Hz, H-3), and 9.93 (1H, br, NH). Found: *m*/*z* 211.0656. Calcd for $C_{13}H_9NO_2$: M, 211.0633.

Benzo[*b*]cyclohept[*e*][1,4]oxazin-8(11*H*)-one (8): Brown needles; mp>300 °C (from MeOH); UV_{max} (MeOH) 222 (log ε 4.12), 266 (4.34), 275 (4.32), 318 (3.39 sh), and 420 nm (4.02), (MeOH+6 M HCl) 227 (log ε 4.25), 266 (4.29), 275 (4.31), 330 (3.60), 443 (3.81), and 466 nm (3.79 sh), (DMSO) 268, 277, 315, and 408 nm, ($CHCl_3$) 264, 274, 320 (sh), and 402 nm; IR (KBr) 3250—2800 and 1644 cm^{-1}; ^{1}H NMR (270 MHz, DMSO-*d*$_6$) δ=6.36 (1H, dd, *J*=12.7 and 2.0 Hz, H-7), 6.43 (1H, dd, *J*=8.0 and 2.0 Hz, H-4), 6.52 (1H, dd, *J*=8.0 and 2.0 Hz, H-1), 6.64 (1H, td, *J*=8.0 and 2.0 Hz, H-3), 6.69 (2H, m, H-9,10), 6.73 (1H, td, *J*=8.0 and 2.0 Hz, H-2), 6.75 (1H, d, *J*=12.7 Hz, H-6), and 8.70 (1H, br, NH); ^{1}H NMR (270 MHz, CD_3OD) δ=6.57 (1H, dd, *J*=13.1 and 2.5 Hz, H-7), 6.77 (1H, d, *J*=13.1 Hz, H-10), 6.84 (1H, dd, *J*=13.1 and 2.5 Hz, H-9), and 6.89 (1H, d, *J*=13.1 Hz, H-6); ^{13}C NMR (67.8 MHz, DMSO-*d*$_6$) δ=114.3 (d), 114.9 (d), 123.7 (d), 124.9 (d), 129.5 (d), 129.6 (d), 130.0 (s), 131.1 (d), 138.8 (d), 139.7 (s), 143.2 (s), 143.4 (s), and 179.5 (s). Found: C, 73.76; H, 3.99; N, 6.28%; M$^+$, 211. Calcd for $C_{13}H_9NO_2$: C, 73.92; H, 4.29; N, 6.63%; M, 211.

Benzo[*b*]cyclohept[*e*][1,4]oxazin-9(11*H*)-one (9): Yellow needles; mp 243—245 °C (from MeOH); UV_{max} (MeOH) 239 (log ε 4.19), 294 (4.48 sh), 307 (4.55), 338 (4.00 sh), 373 (3.77), and 394 nm (3.77), (MeOH+6 M HCl) 226 (log ε 4.14), 251 (4.22), 257 (4.24), 289 (4.36), 308 (4.54), and 426 nm (3.94), (MeOH+6 M NaOH) 240 (log ε 3.99), 305 (4.54), 324 (4.27 sh), 340 (4.07 sh), 423 (4.09), and 453 nm (3.91 sh), (DMSO) 298, 308, 340 (sh), and 380 nm (sh), ($CHCl_3$) 296, 307, 340 (sh), and 394 nm (sh); IR (KBr) 3250 and 1614 cm^{-1}; ^{1}H NMR (270 MHz, DMSO-*d*$_6$) δ=6.05 (1H, d, *J*=2.5 Hz, H-10), 6.32 (1H, dd, *J*=12.4 and 2.5 Hz, H-8), 6.39 (1H, d, *J*=10.3 Hz, H-6), 6.70 (1H, dd, *J*=12.4 and 10.3 Hz, H-7), 6.71 (1H, dd, *J*=8.0 and 1.5 Hz, H-4), 6.78 (1H, td, *J*=7.5 and 1.5 Hz, H-2), 6.83 (1H, dd, *J*=8.0 and 1.5 Hz, H-1), 6.88 (1H, td, *J*=7.5 and 1.5 Hz, H-3), and 9.80 (1H, br, NH); ^{13}C NMR (67.8 MHz, DMSO-*d*$_6$) δ=114.0 (d), 114.2 (d), 114.8 (d), 115.2 (d), 121.8 (d), 124.2 (d), 127.1 (s), 132.2 (d), 136.3 (d), 140.8 (s), 141.5 (s), 151.0 (s), and 183.1 (s). Found: C, 73.61; H, 4.38; N, 6.30%; M$^+$, 211. Calcd for $C_{13}H_9NO_2$: C, 73.92; H, 4.29; N, 6.63%; M, 211.

Benzo[*b*]cyclohept[*e*][1,4]oxazin-10(11*H*)-one (10): Mp 171—172 °C (lit,[4] mp 170 °C); UV_{max} (DMSO) 265, 273, 312, 330, 406, and 487 nm, ($CHCl_3$) 261, 271, 305, 324, 404, and 483 nm; ^{1}H NMR (270 MHz, DMSO-*d*$_6$) δ=6.57 (1H, dd, *J*=8.0 and 2.0 Hz, H-4), 6.68 (2H, m, H-3,7), 6.73 (1H, td, *J*=8.0 and 2.0 Hz, H-2), 6.78 (1H, dd, *J*=11.1 and 1.2 Hz, H-6), 6.93 (1H, dd, *J*=8.0 and 2.0 Hz, H-1), 6.94 (1H, dd, *J*=11.4 and 1.5 Hz, H-9), 7.03 (1H, ddd, *J*=11.4, 8.3, and 1.5 Hz, H-8), and 8.85 (1H, br, NH); ^{13}C NMR (67.8 MHz, DMSO-*d*$_6$) δ=114.4 (d), 115.5 (d), 123.8 (d), 124.6 (d), 125.2 (d), 128.2 (d), 129.3 (s), 133.9 (d), 134.2 (d), 141.4 (s), 143.7 (s), 146.5 (s), and 171.9 (s).

Acetylation of 6—10. A mixture of **9** (10 mg, 0.05 mmol) and acetic anhydride (0.6 cm^3) in acetic acid (1 cm^3) containing a trace amount of concd sulfuric acid was stirred for 2 h at room temperature, followed by the same procedures as those described above for **11b**. The residual solid was recrystallized from MeOH to give **22d** (10 mg, 83% yield). Similarly, **22a** (80% yield), **22b** (80% yield), and **22c** (80% yield) were obtained from **6**, **7**, and **8**, respectively. Compound **10** was recovered unchanged under similar conditions.

6-Acetoxybenzo[*b*]cyclohept[*e*][1,4]oxazine (22a): Brown needles; mp 120—122 °C (from MeOH); UV_{max} (MeOH) 259 (log ε 4.33), 267 (4.30), 300 (3.80), 316 (3.70 sh), 330 (3.54 sh), and 405 nm (3.99), (MeOH+6 M HCl) 225 (log ε 4.35), 263 (4.29), 271 (4.33), 319 (3.84), 431 (3.91), and 453 nm (3.88 sh); IR (KBr) 1770 cm^{-1} (C=O); ^{1}H NMR (270 MHz, CD_3CN) δ=2.19 (3H, s, Me), 5.89 (1H, ddd, *J*=12.4, 6.4, and 2.5 Hz, H-8), 5.98 (1H, dd, *J*=12.4 and 2.0 Hz, H-7), 6.19 (1H, dd, *J*=12.5 and 2.5 Hz, H-10), 6.23 (1H, ddd, *J*=12.5, 6.4, and 2.0 Hz, H-9), 6.50 (1H, m, H-4), and 6.82 (3H, m, H-1,2,3). Found: C, 70.92; H, 4.65; N, 5.34%; M$^+$, 253. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53%; M, 253.

7-Acetoxybenzo[*b*]cyclohept[*e*][1,4]oxazine (22b); Brown

needles; mp 95—97 °C (from MeOH); UV_{max} (MeOH) 259 (log ε 4.17), 268 (4.12), 294 (3.95), and 410 nm (3.94), (MeOH+6 M HCl) 225 (log ε 4.27), 261 (4.17), 272 (4.12), 311 (3.82), 429 (3.77), and 457 nm (3.75 sh); IR (KBr) 1755 cm^{-1} (C=O); ^1H NMR (270 MHz, CD_3CN) δ=2.14 (3H, s, Me), 5.60 (1H, d, *J*=2.0 Hz, H-6), 5.84 (1H, dd, *J*=10.0 and 2.0 Hz, H-8), 6.37 (1H, dd, *J*=12.0 and 10.0 Hz, H-9), 6.47 (2H, m, H-4,10), and 6.80 (3H, m, H-1,2,3). Found: *m/z* 253.0737. Calcd for $C_{15}H_{11}NO_3$: M, 253.0737.

8-Acetoxybenzo[*b*]cyclohept[*e*][1,4]oxazine (22c): Brown needles; mp 139—141 °C (from MeOH); UV_{max} (MeOH) 260 (log ε 4.36), 269 (4.32), 300 (3.82), 320 (3.70 sh), 334 (3.66 sh), and 415 nm (4.05), (MeOH+6 M HCl) 225 (log ε 4.35), 263 (4.38), 272 (4.41), 323 (3.87), 441 (3.97), and 467 nm (3.93 sh); IR (KBr) 1750 cm^{-1} (C=O); ^1H NMR (270 MHz, CD_3CN) δ=2.10 (3H, s, Me), 5.40 (1H, d, *J*=10.1 Hz, H-6), 5.77 (1H, dd, *J*=10.1 and 2.7 Hz, H-7), 6.00 (1H, dd, *J*=12.7 and 2.7 Hz, H-9), 6.10 (1H, d, *J*=12.7 Hz, H-10), 6.42 (1H, m, *J*=8.0 and 2.0 Hz, H-4), and 6.77 (3H, m, H-1,2,3). Found: *m/z* 253.0721. Calcd for $C_{15}H_{11}NO_3$: M, 253.0737.

9-Acetoxybenzo[*b*]cyclohept[*e*][1,4]oxazine (22d): Brown needles; mp 149—151 °C (from MeOH); UV_{max} (MeOH) 260 (log ε 4.49), 268 (4.39), 295 (3.94), and 410 nm (4.07), (MeOH+6 M HCl) 226 (log ε 4.29), 262 (4.32), 272 (4.37), 315 (4.00), 432 (3.95), and 457 nm (3.91 sh); IR (KBr) 1743 cm^{-1} (C=O); ^1H NMR (270 MHz, CD_3CN) δ=2.12 (3H, s, Me), 5.40 (1H, d, *J*=9.6 Hz, H-6), 5.57 (1H, dd, *J*=11.6 and 2.6 Hz, H-8), 5.79 (1H, d, *J*=2.6 Hz, H-10), 6.02 (1H, dd, *J*=11.6 and 9.6 Hz, H-7), 6.44 (1H, dd, *J*=8.0 and 2.0 Hz, H-4), and 6.66—6.88 (3H, m, H-1,2,3). Found: C, 70.85; H, 4.55; N, 5.29%; M^+, 253. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53; M, 253.

Methylation of 6—10. Ethereal diazomethane (0.5 mmol) was added to a solution of **9** (10 mg, 0.05 mmol) in ether (2 cm^3) and the mixture was stirred for 24 h at room temperature. After removal of the ether, the residue was recrystallized from benzene to give **25d** (10 mg, 80% yield). Similarly, **25a** (70% yield), **25b** (70% yield), and **25c** (80% yield) were obtained from **6**, **7**, and **8**, respectively. Compound **10** was recovered unchanged under similar conditions.

6-Methoxybenzo[*b*]cyclohept[*e*][1,4]oxazine (25a): Brown needles; mp 94—96 °C (from benzene); UV_{max} (MeOH) 263, 269, 312, and 415 nm, (MeOH+6 M HCl) 230, 275, 310, and 436 nm; ^1H NMR (270 MHz, CD_3CN) δ=3.68 (3H, s, OMe), 6.08 (1H, ddd, *J*=12.0, 6.5, and 3.0 Hz, H-8), 6.34 (2H, m, H-7,9), 6.39 (1H, d, *J*=12.0 Hz, H-10), 6.49 (1H, m, H-4), and 6.74—6.85 (3H, m, H-1,2,3). Found: *m/z* 225.0771. Calcd for $C_{14}H_{11}NO_2$: M, 225.0790.

7-Methoxybenzo[*b*]cyclohept[*e*][1,4]oxazine (25b): Brown needles; mp 87—89 °C (from benzene); UV_{max} (MeOH) 222, 260, 268, 325, and 414 nm, (MeOH+6 M HCl) 226, 261, 271, 310, 430, and 467 nm (sh); ^1H NMR (270 MHz) δ=3.66 (3H, s, OMe), 5.65 (1H, d, *J*=1.5 Hz, H-6), 5.92 (1H, dd, *J*=12.5 and 9.7 Hz, H-9), 6.10 (1H, d, *J*=12.5 Hz, H-10), 6.25 (1H, dd, *J*=9.7 and 1.5 Hz, H-8), 6.49 (1H, m, H-4), and 6.74—6.86 (3H, m, H-1,2,3); MS (70 °C) *m/z* 225 (M^+, 64%), 210 (M^+—Me, 24%), and 182 (M^+—Me—CO, 100%). Found: *m/z* 225.0763. Calcd for $C_{14}H_{11}NO_2$: M, 225.0790.

8-Methoxybenzo[*b*]cyclohept[*e*][1,4]oxazine (25c): Brown needles; mp 105—107 °C (from benzene); UV_{max} (MeOH) 220, 263, 272, 320, and 427 nm, (MeOH+6 M HCl) 228, 265, 271, 300, 325, 440, and 510 nm (sh); ^1H NMR (270 MHz) δ=3.58 (3H, s, OMe), 5.35 (1H, dd, *J*=10.3 and 2.0 Hz, H-7), 5.51 (1H, d, *J*=10.3 Hz, H-6), 6.12 (1H, dd, *J*=13.0 and 2.0 Hz, H-9), 6.28 (1H, d, *J*=13.0 Hz, H-10), 6.34 (1H, dd, *J*=7.5 and 1.5 Hz, H-4), and 6.64—6.81 (3H, m, H-1,2,3). Found: *m/z* 225.0793. Calcd for $C_{14}H_{11}NO_2$: M, 225.0790.

9-Methoxybenzo[*b*]cyclohept[*e*][1,4]oxazine (25d): Brown needles; mp 89—91 °C (from benzene); UV_{max} (MeOH) 224 (log ε 4.09), 258 (4.39), 267 (4.44), 350 (3.99 sh), 412 (4.08), and 448 nm (3.72 sh), (MeOH+6 M HCl) 225 (log ε 4.13), 252 (4.25), 259 (4.30), 287 (4.32), 305 (4.21), and 432 nm (3.94); ^1H NMR (270 MHz) δ=3.64 (3H, s, OMe), 5.44 (1H, d, *J*=9.7 Hz, H-6), 5.69 (2H, m, H-8,10), 5.99 (1H, dd, *J*=12.3 and 9.7 Hz, H-7), 6.47 (1H, m, H-4), and 6.72—6.86 (3H, m, H-1,2,3). Found: C, 74.35; H, 5.06; N, 5.93%; M^+, 225. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22%; M, 225

Hydrolysis of 22a—d. Similar procedures as those described above for compounds **11a—e** were followed. Thus, the treatment of **22a—d** (ca. 5 mg) with AcOH (2 cm^3) at 100 °C for 5—15 min gave **6—9**, respectively, in an almost quantitative yield.

Hydrolysis of 25a—d. Solutions of **25a—d** (ca. 2 mg) in methanol (5 cm^3) were allowed to stand for 48 h at room temperature. After removal of the solvent in vacuo, the residue was recrystallized from methanol, giving **6—9** in an almost quantitative yield.

Hydrolysis of 15. A solution of **15**[6] (50 mg) in acetic acid (10 cm^3) was heated at 110 °C for 10 h. The reaction mixture was chromatographed over thin-layer plates with benzene–MeOH (10:1) as the eluent, giving **16** (2 mg, 5% yield), **17** (34 mg, 80% yield), and **12d**[6] (trace).

8-Bromobenzo[*b*]cyclohept[*e*][1,4]oxazin-6(11*H*)-one (16): Brown solid; UV_{max} (MeOH) 230, 260, 300, 320 (sh), and 400 nm; MS (70 °C): *m/z* 291 (M^+, 15%), 289 (M^+, 17%), 263 (M^+—CO, 71%), 261 (M^+—CO, 65%), 182 (67%), and 154 (100%). Found: *m/z* 290.9741 and 288.9739 (1:1). Calcd for $C_{13}H_8NO_2Br$: M, 290.9718 and 288.9738.

6-Bromobenzo[*b*]cyclohept[*e*][1,4]oxazin-8(11*H*)-one (17): Brown solid; UV_{max} (MeOH) 250, 275, 315, and 410 nm, (MeOH+6 M HCl) 236, 264, 270, 320, and 435 nm, (MeOH+6 M NaOH) 238, 265, 275, 320, 463, and 495 nm (sh). Found: *m/z* 290.9759 and 288.9741 (1:1). Calcd for $C_{13}H_8NO_2Br$: M, 290.9718 and 288.9738.

Acetylation of 16 and 17. Acetylation of **16** and **17** was conducted in a manner similar to that described above for **6—10**, and gave **23** and **24**, respectively, in an almost quantitative yield.

6-Acetyloxy-8-bromobenzo[*b*]cyclohept[*e*][1,4]oxazine (23): Brown needles; mp 139—140 °C (from benzene); UV_{max} (MeOH) 220 (log ε 4.33), 258 (4.40), 269 (4.32), 294 (3.94), 305 (3.94), 319 (3.89 sh), and 409 nm (4.08), (MeOH+6 M HCl) 232 (log ε 4.29), 263 (4.40), 270 (4.42), 325 (3.95), 445 (4.03), and 472 nm (3.98 sh); IR (KBr) 1770 cm^{-1} (C=O); ^1H NMR (270 MHz) δ=2.22 (3H, s, Me), 6.05 (1H, d, *J*=13.0 Hz, H-10), 6.27 (1H, d, *J*=2.0 Hz, H-7), 6.28 (1H, dd, *J*=13.0 and 2.0 Hz, H-9), 6.41 (1H, m, H-4), and 6.76—6.90 (3H, m, H-1,2,3). Found: *m/z* 330.9792 and 332.9832 (1:1). Calcd for $C_{15}H_{10}NO_3Br$: M, 330.9844 and 332.9824.

8-Acetyloxy-6-bromobenzo[*b*]cyclohept[*e*][1,4]oxazine (24): Brown needles; mp 110—111 °C (from benzene); UV_{max} (MeOH) 259 (log ε 4.25), 268 (4.23), 307 (3.76), 320 (3.71 sh), and 410 nm (3.90), (MeOH+6 M HCl) 227 (log ε 4.27), 263 (4.42), 270 (4.24), 321 (3.81), 441 (3.82), and 471 nm (3.77 sh); IR (KBr) 1750 cm^{-1} (C=O); ^1H NMR (270 MHz) δ=2.17 (3H, s,

Me), 5.89 (1H, dd, J=13.0 and 2.2 Hz, H-9), 6.18 (1H, d, J=13.0 Hz, H-10), 6.22 (1H, d, J=2.2 Hz, H-7), 6.60 (1H, dd, J=8.0 and 2.0 Hz, H-4), 6.78—6.94 (3H, m, H-1,2,3). Found: C, 54.50; H, 3.27; N, 3.95%; M^+, 332. Calcd for $C_{15}H_{10}NO_3Br$: C, 54.24; H, 3.03; N, 4.22%; M, 332.

Hydrolysis of 18. A solution of **18**[9] (25 mg) in acetic acid (5 cm^3) was heated at 110 °C for 5 h, followed by the same procedures as those described above for **15**, and produced **19** (13 mg, 60% yield) and **20** (4 mg, 20% yield).

7,9-Dibromobenzo[*b*]cyclohept[*e*][1,4]oxazin-10(11*H*)-one (19): Reddish-violet needles; mp 256—257 °C (from benzene); UV_{max} (MeOH) 256 (log ε 4.42), 272 (4.26 sh), 302 (4.20), 339 (3.79 sh), 418 (3.51 sh), and 520 nm (4.08), (MeOH+6 M NaOH) 260 (log ε 4.31), 274 (4.25), 304 (4.16), and 503 nm (4.16); IR (KBr) 3270 and 1557 cm^{-1}; ^{1}H NMR (100 MHz) δ=6.43—6.82 (4H, m, H-1,2,3,4), 7.62 (1H, d, J=2.0 Hz, H-6), and 8.08 (1H, d, J=2.0 Hz, H-8); MS (140 °C): m/z 370 (M^+, 50%), 368 (M^+, 100%), and 366 (M^+, 51%). Found: C, 42.41; H, 2.12; N, 3.59%. Calcd for $C_{13}H_7NO_2Br_2$: C, 42.31; H, 1.91; N, 3.80%. Compound **19** was also obtained (90 mg, 90% yield) by heating **21**[16] (100 mg, 0.27 mmol) with **4** (50 mg, 0.46 mmol) in ethanol (3 cm^3) at 60 °C for 2 h, followed by the same procedures as those described above for **12c**.

6,8-Dibromobenzo[*b*]cyclohept[*e*][1,4]oxazin-10(11*H*)-one (20): Reddish-violet solid; UV_{max} (MeOH) 225, 260, 270 (sh), 320, 420, and 510 nm; ^{1}H NMR (270 MHz) δ=6.54 (2H, m, H-2,4), 6.77 (2H, m, H-1,3), 7.12 (1H, d, J=1.8 Hz, H-9), 7.84 (1H, br, NH), and 8.08 (1H, d, J=1.8 Hz, H-7). Found: m/z 370.8789, 368.8847, and 366.8838 (1:2:1). Calcd for $C_{13}H_7NO_2Br_2$: M, 370.8804, 368.8824, and 366.8844.

Reduction of 19 and 20 Zinc dust (20 mg) was added to a solution of **19** (30 mg, 0.08 mmol) in acetic acid (5 cm^3), and the mixture was stirred at room temperature for 2 h. The reaction mixture was filtered and evaporated to dryness in vacuo. The residue was then chromatographed on silica-gel thin layer plates with benzene–MeOH (50:1) as the eluent, giving compound **10**[4] (40% yield). Compound **10** was also obtained from **20** by following an identical procedure.

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