5 h, poured into ice and water (400 mL), and extracted with CH_2Cl_2 (500 mL). The organic layer was dried over Na_2SO_4, and the solvent was evaporated off to give 119.0 mg (94%) of pure **10A**, mp 104 °C (recrystallized from *n*-hexane; colorless needles). ^1H NMR: δ 7.541 (s, 2 H), 7.502 (d, 2 H, 7.70), 7.135 (d, 2 H, 8.1), 4.784 (s, 1 H), 3.7059 (3 H, s), 2.438 (6 H, s). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39; N, 0.0. Found: C, 80.63; H, 6.19; N, 0.0.

Reaction of α-(Methoxycarbonyl)bis(*p*-methylphenyl)methanol in TFA. To 6.1 mL (200 equiv) of TFA cooled at 0 °C in an ice water bath was added 105.0 mg (0.4 mmol) of **4A** in portions with vigorous stirring. The orange solution was stirred for 0.5 h at 0 °C and subsequently at ambient temperature for 1.75 h. The solution was poured into ice and water (400 mL) and extracted with CH_2Cl_2 (400 mL). The organic layer was dried over Na_2SO_4, and the solvent was evaporated off to give 111.9 mg of the residue, which was flash chromatographed (CH_2Cl_2–*n*-hexane, 1:2) to give 35.9 mg (25%) of α-(methoxycarbonyl)bis(*p*-methylphenyl)methyl trifluoroacetate as a nonpolar fraction and 66.3 mg (63%) of recovered **4A**. α-(Methoxycarbonyl)bis(*p*-methylphenyl)methyl trifluoroacetate: ^1H NMR: 7.289 (d, 4 H, 8.42), 7.143 (d, 4 H), 3.845 (s, 3 H), 2.350 (s, 6 H).

Reaction of α-Carboxybis(*p*-methylphenyl)methanol in TFSA. An aliquot of 4.4 mL (100 equiv) of TFSA was cooled to −20 °C in a dry ice–ethanol bath, and then α-carboxybis(*p*-methylphenyl)methanol (**4B**) (178.8 mg) was added in portions with vigorous stirring. The solution was stirred for 2 h before usual aqueous workup as described above. The crude residue was again dissolved in CH_2Cl_2 (100 mL) and washed with 2 N NaOH (200 mL). The aqueous layer was acidified with concentrated HCl and extracted with CH_2Cl_2 (300 mL). The solvent was evaporated to give 136.3 mg (82%) of pure **10B**: mp 241–242 °C (recrystallized from *n*-hexane–CH_2Cl_2). ^1H NMR: δ 7.538 (s, 2 H, $H_{4,5}$), 7.519 (d, 2 H, 7.7), 7.136 (d, 2 H, 7.7), 4.783 (s, 1 H, H_9), 2.437 (s, 6 H). ^{13}C NMR ($CDCl_3$ + DMSO-d_6): δ 174.5 (s, C_{10}), 141.2 (s), 138.9 (s), 137.0 (s), 127.7 (d, 158.5), 125.1 (d, 161.4), 119.91 (d, 155.1), 21.2 (q, 126.2). The structure was confirmed after methyl esterification. The IR and NMR spectra were in good accordance with those of an authentic sample.

Reaction of α-(*p*-Methylbenzoyl)bis(*p*-methylphenyl)methanol in TFSA. To 10.6 mL (200 equiv) of TFSA cooled at 0 °C in an ice bath was added α-(p-methylbenzoyl)bis(*p*-methylphenyl)methanol (**4C**) (198.1 mg, 0.6 mmol) in portions with vigorous stirring. The purple-red solution was stirred at 0 °C for 3 h and poured into ice and water (400 mL). The crude residue obtained by usual extraction was purified by flash column chromatography with the solvent CH_2Cl_2–*n*-hexane (1:4) to give 130.4 mg (70%) of the fluorene **10C** and 26.0 mg (14%) of the phenanthrol **11C**. **10C**: mp 160–161.5 °C, colorless needles (recrystallized from *n*-hexane). ^1H NMR: δ 7.636 (2 H, d, 8.43), 7.625 (2 H, s), 7.246 (2 H, d, 9.15), 7.144 (2 H, d, 8.01), 7.059 (2 H, d, 7.7), 5.487 (s, 1 H), 2.444 (6 H, s), 2.351 (3 H, s). ^{13}C NMR: δ 197.91 (s), 143.85 (s), 141.69 (s), 140.08 (s), 137.66 (s), 133.98 (s), 129.19 (s), 128.26 (d), 124.76 (d), 120.93 (d), 58.23 (d), 21.57 (q). Anal. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45; N, 0.0. Found: C, 88.16; H, 6.56; N, 0.0. **11C**: oily material. Mass: *m/e* 312. ^1H NMR δ 8.483 (s, 1 H, H_4), 8.442 (s, 1 H, H_5), 8.241 (d, 1 H, H_2, 8.42), 7.472 (d, 1 H, H_1, 8.06), 7.410 (d, 2 H, H_3, 7.7), 7.344 (d, 2 H, H_m, 7.69), 7.294 (d, 1 H, H_7, 8.43), 7.238 (d, 1 H, H_8, 8.43), 5.370 (s), 2.647 (3 H, s, CH_3^3), 2.567 (3 H, s, CH_3^6), 2.490 (3 H, s, CH_3^p). ^{13}C NMR: δ 145.48 (s), 138.24 (s), 136.64 (s), 133.13 (s), 131.53 (s), 130.77 (d), 130.65 (d), 130.42 (d), 128.29 (d), 128.17 (d), 126.19 (s), 125.28 (d), 123.00 (s), 122.86 (d), 122.36 (d), 122.27 (d), 22.12 (q), 21.71 (q), 21.36 (q).

Reaction of Benzoin in TFSA. Benzoin **14** (106.9 mg) was added in portions to well-stirred TFSA (8.8 mL, 200 equiv) cooled at 0–5 °C in an ice water bath. After stirring at 0–5 °C for 45 min, usual aqueous workup was carried out. The residue obtained by the usual extraction procedure (with CH_2Cl_2) was flash chromatographed (AcOEt–*n*-hexane, 1:5) to give 11.1 mg (11%) of **16** as a major product. The yield was not optimized. **16**: ^1H NMR: δ 8.673 (dd, 1 H, 8.06, 1.46), 8.5854 (dd, 1 H, 1.83, 8.25), 8.312 (dd, 1 H, 1.47, 8.06), 7.717–7.676 (m, 2 H), 7.646 (dt, 1 H, 1.47, 7.44). The IR and NMR spectra of the product were identical with those of authentic **16**.

Reaction of α-(*p*-Methoxybenzoyl)bis(*p*-methoxyphenyl)methanol in TFA. A solution of α-(*p*-methoxybenzoyl)bis(*p*-methoxyphenyl)methanol (**3C**) (75.6 mg, 0.2 mmol) in TFA (200 equiv, 3.54 mL) was heated at 70 °C for 1.25 h and then poured into ice and water (400 mL). The mixture was extracted with CH_2Cl_2 (500 mL), and the solvent was evaporated. The residue was flash chromatographed with the solvent CH_2Cl_2–*n*-hexane (1:1) to give 68.9 mg (96%) of the benzofuran **18**, mp 85.5–87.5 °C (recrystallized from *n*-hexane). ^1H NMR: δ 7.552 (dd, 2 H, 6.96, 2.2), 7.394 (d, 2 H, 8.79), 7.317 (d, 1 H, 8.42), 7.0562 (d, 1 H, 2.2), 6.975 (d, 2 H, 8.79), 6.841 (dd, 1 H, 9.89, 2.2), 6.825 (d, 2 H, 9.16), 3.853 (6 H, s), 3.849 (3 H, s). ^{13}C NMR: δ 159.26 (s), 158.91 (s), 158.03 (s), 154.7 (s), 149.54 (s), 130.77 (d, 158.5), 127.9 (d, 161.4), 125.22 (s), 124.03 (s), 123.71 (s), 119.85 (d, 161.4), 115.47 (s), 114.36 (d, 161.4), 113.84 (d, 161.4), 111.53 (d, 161.4), 95.68 (d, 164.4), 55.72 (q, 143.7), 55.22 (q, 143.8). Anal. Calcd for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59; N, 0.0. Found: C, 76.44; H, 5.62; N, 0.0.

Reaction of α-(*p*-Methoxybenzoyl)bis(*p*-methoxyphenyl)methanol in TFSA. A solution of **3C** (76.5 mg, 0.2 mmol) in TFSA (3.5 mL, 200 equiv) was heated at 70 °C for 4 h and submitted to the usual aqueous workup. Purification by flash column chromatography (CH_2Cl_2–*n*-hexane) gave 2.1 mg (3%) of the benzofuran **18** and the 40 mg (52%) of the starting material **3C**.

NMR Spectroscopic Evidence for a Twin-Chair Conformer in Quinoxaline-Annelated Bicyclo[4.4.1]undecanones

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In NMR spectra at low temperature, it was found that diquinoxalino-, quinoxalinobenzo-, and quinoxalinonaphtho-annelated bicyclo[4.4.1]undeca-3,8-dien-11-ones, **1** and **5**, exist in equilibrium among two chair–boat conformers and a twin-chair one, which was not detected in the spectra of the corresponding dibenzo, benzonaphtho, and dinaphtho analogues.

Previously, we have reported[2] that dibenzo- and dinaphtho-annelated bicyclo[4.4.1]undecan-11-ones invert between two chair–boat conformers, and that, from the measured $\Delta G^{\ddagger}$ values (10–15 kcal/mol), their inversion

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Scheme I

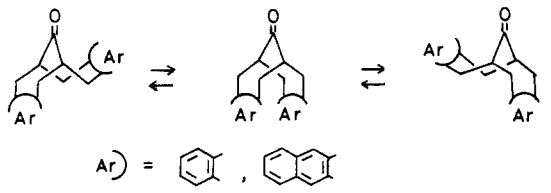


Table I. ^{1}H NMR Spectral Data of 6a–c in $CDCl_3$

compound	ring[a]	aromatic protons, δ ppm
6a	Q–Q	7.1–7.3 (4 H, m), 7.3–7.6 (4 H, m)
6b	Q–B	6.1–6.3 (2 H, m), 6.6–6.8 (2 H, m), 7.4–7.6 (4 H, m)
6c	Q–N	6.8–7.0 (2 H, m), 7.05–7.24 (4 H, m), 7.16 (2 H, br s), 7.3–7.5 (2 H, m)
2,3-diMe-Q[b]	Q	7.45–7.65 (2 H, m), 7.8–7.95 (2 H, m)
1,2-diMe-B[c]	B	7.03 (4 H, br s)
2,3-diMe-N[d]	N	7.15–7.35 (2 H, m), 7.43 (2 H, br s), 7.50–7.7 (2 H, m)

[a] Letters Q, B, N mean quinoxaline, benzene, and naphthalene, respectively. [b] 2,3-dimethylquioxaline. [c] o-Xylene. [d] 2,3-Dimethylnaphthalene.

mode is a stepwise process, probably via a twin-chair conformer as an intermediate. MMP2 calculation[3] including phenyl–phenyl interaction revealed the chair–boat form to be more stable than the twin-chair type by 0.9 kcal/mol, while standard MMP2 method estimated the twin-chair conformer more stable than the chair–boat one by 1.6 kcal/mol.

In the course of our study on the effect of aromatic and heteroaromatic rings on the inversion process, we prepared quinoxaline-annelated bicyclo[4.4.1]undecan-11-ones 1 and obtained NMR spectroscopic evidence for the equilibrium among chair–boat, twin-chair, and boat–chair conformers, which is reported herein.

Results and Discussion

Preparation. Dimethyl 11-oxodiquinoxalinobicyclo-[4.4.1]undecandicarboxylate (**1a**) was obtained by the one-pot reaction of 2,3-bis(bromomethyl)quinoxaline (**2**) with dimethyl 3-oxoglutarate under PTC conditions with Na_2CO_3. Quinoxaline-annelated cycloheptanone **3a** was similarly prepared using $NaHCO_3$ as a base, but the yield was low. Therefore, unsymmetric benzoquinoxalino- and naphthoquinoxalinobicyclo[4.4.1]undecan-11-ones, **1b** and **1c**, were prepared by the reaction of **2** with cycloheptanone **3b**[2] and **3c**,[2] respectively. Diesters **1a–c** were hydrolyzed, giving dicarboxylic acids **4a–c**. As purification of **4** was difficult, decarboxylation was carried out using unpurified **4**, giving the desired ketones **5a–c**, albeit with low yields.

Although ethylene glycol did not give the expected acetals, ethane-1,2-dithiol gave the corresponding dithioacetals **6a–c** (Scheme II) in the reaction with **5a–c**. In the ^{1}H NMR spectra of **6**, which has two facing aromatic rings in proximity, aromatic protons appeared in a higher field than those of 2,3-dimethylquinoxaline, o-xylene, and 2,3-dimethylnaphthalene (Table I).

NMR Spectral Study of 1 and 5. As already reported,[2] dibenzo- and dinaphthobicyclo[4.4.1]undecan-11-ones invert between two equivalent chair–boat conformers, probably via the twin-chair conformer on the basis of the observed $\Delta G^{\ddagger}$ value of their inversion. Compounds **1** and **5** are flexible as expected, and their ^{1}H and ^{13}C NMR spectra are temperature-dependent, as shown in Figures 1 and 2.

Table II. ^{13}C NMR Data of 1a and 6–10

		chemical shift of methylene		
			chair–boat	
compd	ring[a]	twin-chair	chair form	boat form
1a[b]	Q–Q	43.23 (or 41.65)	41.65 (or 43.23)	38.44
6a	Q–Q	42.41		
6b	B–Q	40.13, 43.00		
6c	N–Q	40.25, 42.94		
7[c,d]	B–N		40.00	35.28, 35.63
8[d]	B–N	40.54, 40.78		
9[e]	B–B		40.13	35.75
10[e]	N–N		40.19	35.75

[a] Letters Q, B, and N mean quinoxaline, benzene, and naphthalene, respectively. [b] At −25 °C. [c] At 0 °C. [d] Reference 4. [e] Reference 2.

Table III. ^{1}H NMR Spectral Data of 1a, 1b, and 5b in $CDCl_3$ at −50 °C

		δ ppm	
compd	ring[a]	aromatic	methoxy
1a	Q–Q	7.2–7.4 (0.85 H, m), 7.4–7.65 (0.85 H, m), 7.65–8.3 (6.3 H, m)	3.78 (s),[b] 3.97 (s)[b]
1b	Q–B	6.3–6.4 (0.1 H, m), 6.7–6.8 (0.1 H, m), 7.0–7.4 (1.7 H, m), 7.40 (2.0 H, br s), 7.65–8.2 (4.1 H, m)	3.74 (s),[b] 3.82 (s)[b]
5b	Q–B	6.2–6.4 (0.15 H, m), 6.7–6.9 (0.15 H, m), 7.13 (1.1 H, br s), 7.39 (2.6 H, br s), 7.55–8.20 (4.0 H, m)	

[a] Letters Q and B mean quinoxaline and benzene, respectively. [b] Accurate relative intensity could not be determined.

The ^{1}H NMR spectrum of **1a** (in CD_2Cl_2) at 30 °C showed methylene protons as two doublet peaks, methoxy ones as a singlet, and aromatic ones as two multiple peaks, indicating the rapid interconversion among conformers. In the spectrum at −50 °C, though observed peaks are not sharp and the methylene signals are not resolved, two singlets due to the ester methoxy group were observed, and aromatic signals appeared as two sets of multiplet peaks. These suggest that, in addition to two chair–boat conformers (B and C) of **1a**, a twin-chair or twin-boat one is spectroscopically observed (Scheme III). Of the two, the twin-chair conformer A, which pocesses two facing quinoxaline rings, is expected to show up-field shift of aromatic protons. This is the case for the ^{1}H NMR spectrum of **6** as mentioned above (Table I). Thus, it is reasonable to assign the peaks observed at higher magnetic field (between 7.2 and 7.6 ppm) to the twin-chair conformer A, and those in lower region (between 7.6 and 8.2 ppm) to the chair–boat ones, B and C, respectively.

The VT ^{13}C NMR spectra of **1a** (in CD_2Cl_2) are shown in Figure 2 and gave further evidence for the twin-chair conformer A.

Each of the singlet signals of bridgehead, ester carbonyl and bridging carbonyl carbon split into a set of two singlets at low temperature. This is due to the presence of the conformer other than equivalent chair–boat ones, B and C. The singlet peak of methylene, which was observed at 42.41 ppm at room temperature, split into three singlets (38.44, 41.56, and 43.23 ppm) at −25 °C. Comparing these chemical shifts with those of the chair–boat form of bi-

(1) Department of Molecular Science and Technology.
(2) Mataka, S.; Takahashi, K.; Hirota, H.; Takuma, K.; Kobayashi, H.; Tashiro, M.; Imada, K.; Kuniyoshi, M. J. Org. Chem. 1986, 51, 4618.
(3) Petersson, I.; Liljefors, T. J. Comp. Chem. 1987, 8, 1139.

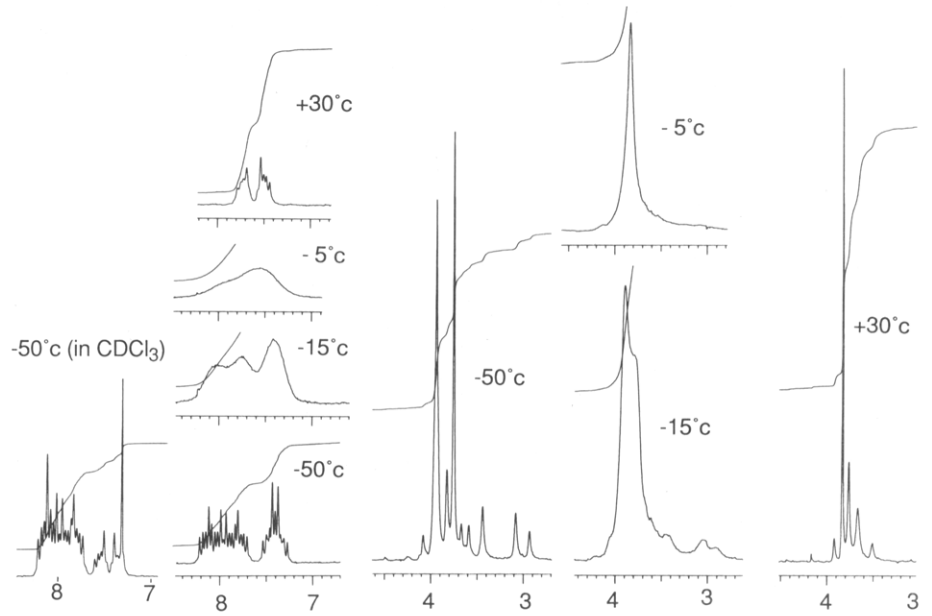
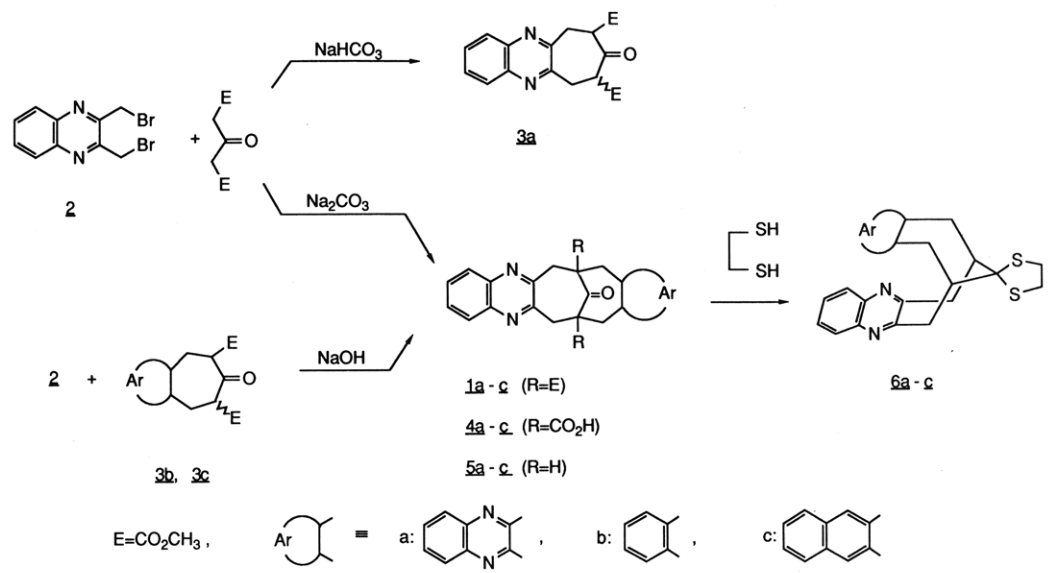
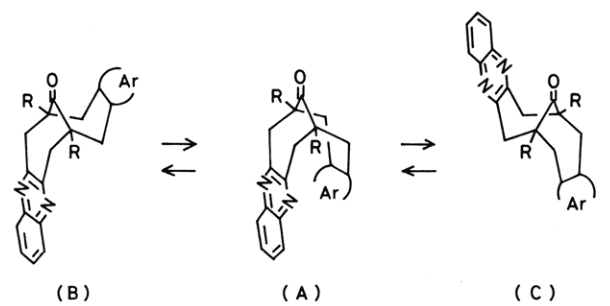


Figure 1. ^{1}H NMR spectra of **1a** in CD_2Cl_2.

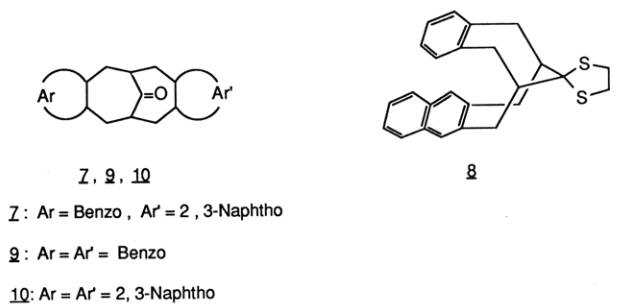
Scheme II



Scheme III



Scheme IV



cyclo[4.4.1]undecanones **7**,[4] **9**,[2] and **10**,[2] and twin-chair type dithioacetals **6** and **8** (Scheme IV and Table II), the benzylic signals at 38.44 ppm is ascribed to the boat-skeleton of B and C, and the other two (41.65 and 43.23 ppm) are to the chair structure of A, B, and C.

The presence of twin-chair conformer was also detected, though in a very small amount, in the ^{1}H NMR spectra of **1b** and **5b** as summarized in Table III.

Interestingly, each of the three conformers, A, B, and C, was observed in the spectra of **5b**. At room temperature, benzene ring protons appeared as a broad single peak at 7.13 ppm, which, at −50 °C, split into two small multiplets

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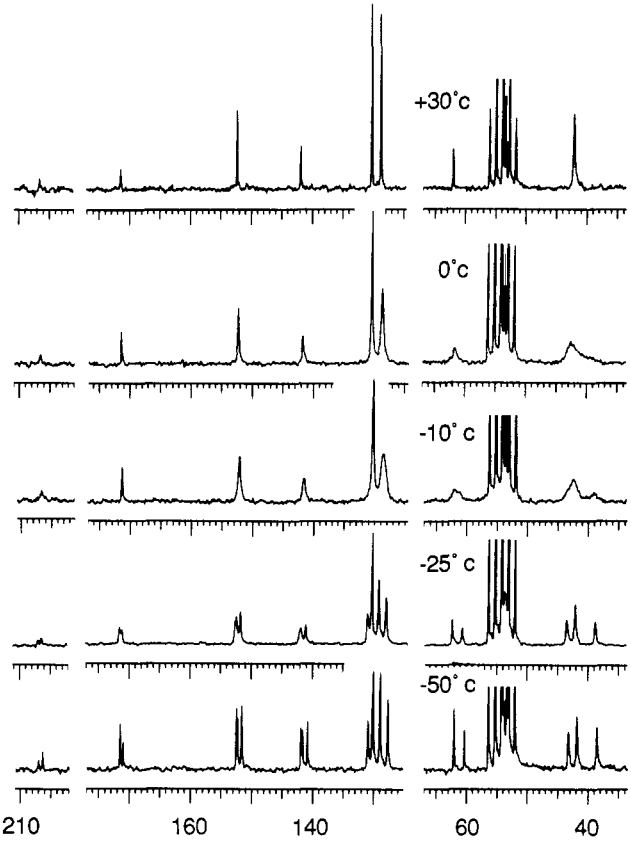

Figure 2. ^{13}C NMR spectra of **1a** in CD_2Cl_2.

Table IV. The Ratio of Twin-Chair Conformer (A) and Chair–Boat Ones (B + C)

compd	solvent	temp, °C	ratio, A/(B + C)
1a	$CDCl_3$	−50	1/2.9
1a	CD_2Cl_2	−50	1/1.6
1b	$CDCl_3$	−50	1/17
5b	$CDCl_3$	−50	1/13

(centered at 6.3 and 6.8 ppm) and two broad singlets (7.13 and 7.39 ppm) (Figure 3). Their relative intensities are 0.15:0.15:1.1:2.6.

The two small peaks are due to twin-chair A. On the chair–boat conformers, it is reasoned that the electron density on benzene ring, which is annelated to the boat structure, is decreased by through-space interaction with the carbonyl group on the bridge. Thus, the peak at 7.13 ppm is tentatively assigned to benzene ring protons of C, while the one at 7.39 ppm may be due to either B or B and C.

The ratios of twin-chair conformer (A) and chair–boat ones (B + C) in **1a**, **1b**, and **5b** were calculated based on ^1H NMR spectra and are given in Table IV. The spectra of **1c**, **5a**, and **5c** at low temperature were not obtained because of a lack of an appropriate solvent.

In $CDCl_3$, whose dielectric constant (4.086)[5] is smaller than that (9.08)[5] of CD_2Cl_2, conformer A is less stabilized by decreasing solvent polarity and, therefore, has a larger dipole[6] than B and C.

It is of interest that the present quinoxaline-annelated bicyclo[4.4.1]undecan-11-ones **1a**, **1b**, and **5b** showed peaks assignable to the twin chair conformers which were not

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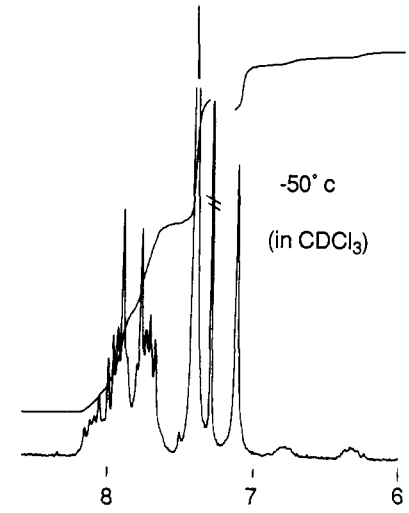

Figure 3. ^1H NMR spectrum of **5b**.

observed in the carbocyclic analogues. This may be reasoned, though not clear at the present time, on the basis of the π–π electronic repulsion between the two facing aromatic rings; such a repulsive interaction between electron-deficient quinoxaline rings seems smaller than those between benzene and naphthalene ones.

In summary, it is concluded that **1a**, **1b**, and **5b** are each in equilibrium among chair–boat (B), twin-chair (A), and boat–chair (C) conformers.

Experimental Section

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded on a Nippon Bunko A-102 spectrophotometer as KBr pellets. ^1H and ^{13}C NMR (internal Me_4Si) spectra were taken on a Nippon Denshi JEOL FT-100 NMR spectrometer in deuteriochloroform unless otherwise stated. Mass spectra were recorded on a Nippon Denshi JMS-01SG-2 mass spectrometer at 75 eV using a direct-inlet system. Column chromatography was carried out on silica gel (Wako gel, C-300).

Dimethyl 3-Oxo-1,2,4,5-tetrahydroquinoxalino[2,3-*d*]cycloheptene-2,4-dicarboxylate (3a). A solution of dimethyl 3-oxoglutarate (1.04 g, 6.0 mmol) in CH_2Cl_2 (15 mL) was added dropwise at room temperature to a mixture of 2,3-bis(bromomethyl)quinoxaline (**2**) (1.02 g, 3.2 mmol), Bu_4NBr (0.62 g, 1.9 mmol), saturated aqueous $NaHCO_3$ (50 mL), and CH_2Cl_2 (25 mL). After the mixture was stirred at room temperature for 17 h, the organic layer was separated, dried, and evaporated in vacuo, yielding a residue which was recrystallized from ethanol to give **3a** as colorless needles (0.25 g, 24%): mp 140–142 °C; IR 1770, 1755, 1740, 1700 cm^{-1}; ^1H NMR δ 3.6–3.9 (m, 6 H) and 3.80 (s, 6 H), 7.0–7.8 (m, 2 H), 7.9–8.2 (m, 2 H); MS *m/e* 328 (M^+). Anal. Calcd for $C_{17}H_{16}N_2O_5$: C, 62.19; H, 4.91; N, 8.53. Found: C, 61.99; H, 4.95; N, 8.52.

Dimethyl 3-Oxo-1,2,4,5-tetrahydrobenzo[*d*]cycloheptene-2,4-dicarboxylate (3b). A modification of the previously reported method[4] gave **3b** in a better yield. To a vigorously stirred mixture of Bu_4NBr (11.2 g, 35 mmol), 5% aqueous $NaHCO_3$ solution (500 mL), and CH_2Cl_2 (50 mL) was added dropwise at room temperature a solution of dimethyl 3-oxoglutarate (18.8 g, 108 mmol) and *o*-xylene dibromide (15.8 g, 60 mmol) in CH_2Cl_2 (150 mL). After 30 h of stirring at room temperature, the reaction mixture was worked up using the same method as for **3a** and recrystallized from hexane to give a 1:2 mixture (mp 80–104 °C) (10.2 g, 72%) of **3b**-1 (mp 93–100 °C) and **3b**-2 (mp 103–110 °C).

Dimethyl 11-Oxoquinoxalino[2,3-*c*]quinoxalino[2′,3′-*h*]bicyclo[4.4.1]undeca-3,8-diene-1,6-dicarboxylate (1a). To a vigorously stirred mixture of **2** (12.0 g, 38 mmol), Bu_4NBr (6.10 g, 19 mmol), 5% aqueous Na_2CO_3 (300 mL), and CH_2Cl_2 (200 mL) was added dropwise at room temperature a CH_2Cl_2 solution (80 mL) of dimethyl 3-oxoglutarate (4.70 g, 27 mmol). After the mixture was stirred at room temperature for 41 h, the organic

layer was separated, washed with water, dried, and evaporated in vacuo leaving a residue, which was washed with a small amount of ethyl acetate and recrystallized from ethanol, giving **1a** as colorless needles (3.65 g, 40%). **3c**: mp 265–267 °C; IR 1740, 1700 cm^{-1}; MS *m/e* 482 (M^+). Anal. Calcd for $C_{27}H_{22}N_4O_5$: C, 67.21; H, 4.60; N, 11.61. Found: C, 66.95; H, 4.67; N, 11.57.

Dimethyl 11-Oxobenzo[*c*]quinoxalino[2,3-*h*]bicyclo-[4.4.1]undeca-3,8-diene-1,6-dicarboxylate (1b). To a vigorously stirred mixture of Bu_4NCl (3.35 g, 12 mmol), 5% aqueous NaOH (100 mL), and CH_2Cl_2 (40 mL) was added dropwise at room temperature a CH_2Cl_2 solution (100 mL) of **3b** (6.54 g, 24 mmol) and **2** (6.38 g, 20 mmol). After the mixture was stirred at room temperature for 1.5 h, the organic layer was separated, washed with water, dried, and evaporated in vacuo, leaving a residue which was washed with a hot 1:1 mixture of benzene and ethyl acetate, giving **1b** as colorless tiny crystals (5.74 g, 66%): mp 242–245 °C; IR 1740, 1695 cm^{-1}; ^1H NMR δ 2.4–4.0 (br peak, 8 H), 3.76 (s, 6 H), 6.8–7.3 (m, 4 H), 7.5–8.1 (m, 4 H); MS *m/e* 430 (M^+). Anal. Calcd for $C_{25}H_{22}N_2O_5$: C, 69.75; H, 5.15; N, 6.51. Found: C, 69.52; H, 5.25; N, 6.49.

Dimethyl 11-Oxonaphtho[2,3-*c*]quinoxalino[2,3-*h*]bicyclo[4.4.1]undeca-3,8-diene-1,6-dicarboxylate (1c). To a vigorously stirred mixture of Bu_4NCl (1.48 g, 5.3 mmol), 5% aqueous NaOH (50 mL), and CH_2Cl_2 (15 mL) was added dropwise at room temperature a CH_2Cl_2 solution (80 mL) of **3c** (3.17 g, 9.7 mmol) and **2** (3.07 g, 9.7 mmol). After the mixture was stirred at room temperature for 2 h, the organic layer was separated, washed with water, dried, and evaporated in vacuo, leaving a residue which was washed with ethyl acetate and recrystallized from acetonitrile, giving a 1:1 complex of **1c** and acetonitrile as colorless prisms [2.86 g, 56%. Anal. Calcd for ($C_{29}H_{24}N_2O_5$ + C_2H_3N): C, 71.38; H, 5.22; N, 8.06. Found: C, 71.24; H, 5.11; N, 7.79]. This complex was dissolved in benzene and evaporated in vacuo to give **1c**: mp 252–254 °C; IR 1740, 1695 cm^{-1}; ^1H NMR δ 2.4–4.2 (br m with br s at 3.76, 14 H), 7.2–8.4 (m, 10 H); MS *m/e* 480 (M^+). Anal. Calcd for $C_{29}H_{24}N_2O_5$: C, 72.49; H, 5.03; N, 5.83. Found: C, 72.52; H, 5.01; N, 5.82.

11-Oxoquinoxalino[2,3-*c*]quinoxalino[2′,3′-*h*]bicyclo-[4.4.1]undeca-3,8-diene-1,6-dicarboxylic Acid Hydrogen Chloride (4a·HCl). After a mixture of **3a** (2.50 g, 5.2 mmol), 20% aqueous Na_2CO_3, and ethanol (30 mL) had been refluxed for 7 h, it was poured into water (600 mL), acidified with dilute hydrochloric acid to pH 2, and allowed to stand overnight. The precipitates were filtered, washed with water, and dried, giving crude **4a**·HCl (2.38 g) as pale yellow solid: mp 230 °C dec; IR 1710 cm^{-1}; MS *m/e* 454 (M^+). Anal. Calcd for $C_{25}H_{18}N_4O_5$·HCl: C, 61.14; H, 3.90; N, 11.41. Found: C, 60.79; H, 3.79; N, 11.26.

11-Oxobenzo[*c*]quinoxalino[2,3-*h*]bicyclo[4.4.1]undeca-3,8-diene-1,6-dicarboxylic Acid (4b). After a mixture of **1b** (3.40 g, 7.9 mmol), 10% aqueous KOH (50 mL), and ethanol (50 mL) had been refluxed for 0.5 h, it was poured into water (100 mL) and acidified with acetic acid to pH 3. The precipitates were filtered, washed with a small amount of water, and stirred in refluxing methanol for 1 h, giving crude **4b** (1.86 g) as colorless powder: mp 265 °C dec; IR 1740 cm^{-1}; MS *m/e* 402 (M^+). Anal. Calcd for $C_{23}H_{18}N_2O_5$: C, 68.65; H, 4.51; N, 6.96. Found: C, 68.13; H, 4.79; N, 6.84.

11-Oxonaphtho[2,3-*c*]quinoxalino[2′,3′-*h*]bicyclo[4.4.1]-undeca-3,8-diene-1,6-dicarboxylic Acid (4c). After a mixture of **3c** (1.90 g, 4.0 mmol), 10% aqueous KOH (30 mL), and ethanol (30 mL) had been refluxed for 2.5 h, it was poured into water (200 mL) and acidified with acetic acid to pH 3. The precipitates were filtered, washed with a small amount of water, and stirred in refluxing methanol for 1 h, giving crude **4c** (0.88 g) as colorless powder: mp 250 °C dec; IR 1720 cm^{-1}; MS *m/e* 452 (M^+). Anal. Calcd for $C_{27}H_{20}N_2O_5$: C, 71.67; H, 4.46; N, 6.19. Found: C, 70.23; H, 4.65; N, 6.12.

Quinoxalino[2,3-*c*]quinoxalino[2′,3′-*h*]bicyclo[4.4.1]-undeca-3,8-dien-11-one (5a). After crude **4a**·HCl (1.82 g) was heated in a mixture of DBU (2.45 g, 16 mmol) and quinoline (15 mL) at 170 °C for 5 h, it was extracted with CH_2Cl_2. The extract was washed continuously with water, dilute hydrochloric acid, and water, dried, and evaporated in vacuo to leave a residue which, on trituration with a mixture of CH_2Cl_2 and benzene, gave crude **5a**. Chromatography using ethyl acetate as an eluent and recrystallization from a mixture of ethyl acetate and benzene gave **5a** as colorless prisms (0.10 g, 7% from **12**): mp 340 °C dec; IR 1700 cm^{-1}; ^1H NMR δ 3.44 (br s, 10 H), 7.54 (m, 4 H), 7.84 (m, 4 H); MS *m/e* 366 (M^+). Anal. Calcd for $C_{23}H_{18}N_4O$: C, 75.39; H, 4.95; N, 15.29. Found: C, 75.86; H, 5.09; N, 14.84.

Benzo[*c*]quinoxalino[2,3-*h*]bicyclo[4.4.1]undeca-3,8-dien-11-one (5b). After a mixture of crude **4b** (300 mg) in *N*,*N*-diethylaniline (10 mL) was heated at reflux under a nitrogen atmosphere for 6 h, it was extracted with benzene. The extract was washed continuously with water, dilute hydrochloric acid, and water, dried, and evaporated in vacuo to leave a residue, which, on trituration with ether, gave crude **5b**. Recrystallization from ethyl acetate gave **5b** as colorless prisms (79 mg, 20% from **3b**): mp 250–252 °C (in a sealed tube); IR 1700 cm^{-1}; ^1H NMR δ 2.98–3.24 (br s, 10 H), 7.12 (br s, 4 H), 7.6–7.7 (m, 2 H), 7.8–8.0 (m, 2 H); MS *m/e* 314 (M^+). Anal. Calcd for $C_{21}H_{18}N_2O$: C, 80.23; H, 5.77; N, 8.91. Found: C, 80.12; H, 5.78; N, 8.87.

Naphtho[2,3-*c*]quinoxalino[2′,3′-*h*]bicyclo[4.4.1]undeca-3,8-dien-11-one (5c). After crude **4c** (880 mg) was heated in a mixture of DBU (1.20 g, 8 mmol) and quinoline (10 mL) at 160 °C for 8 h, it was extracted with CH_2Cl_2. The extract was washed continuously with water, dilute hydrochloric acid, and water, dried, and evaporated in vacuo to leave a residue, which, on trituration with ethanol, gave crude **5c**. Chromatography using a 1:1 mixture of benzene and ethyl acetate as an eluent and recrystallization from ethyl acetate gave **5c** as colorless prisms (94 mg, 20% from **3c**): mp 300 °C; IR 1705 cm^{-1}; ^1H NMR δ 2.8–3.6 (m, 10 H), 7.3–7.5 (m, 2 H), 7.64 (br s, 6 H), 7.8–8.0 (m, 2 H); MS *m/e* 364 (M^+). Anal. Calcd for $C_{25}H_{20}N_2O$: C, 82.37; H, 5.53; N, 7.68. Found: C, 82.24; H, 5.59; N, 7.75.

Quinoxalino[2,3-*c*]quinoxalino[2′,3′-*h*]bicyclo[4.4.1]-undeca-3,8-dien-11-one Ethylene Dithioacetal (6a). A mixture of **5a** (52 mg, 0.14 mmol), ethane-1,2-dithiol (0.5 mL), and BF_3OEt_2 (0.5 mL) in acetic acid (2 mL) was heated at reflux for 3 h. After being cooled, the mixture was poured into ether, and precipitates were collected by filtration. Recrystallization from benzene gave **6a** (11 mg, 18%): colorless tiny crystals; mp 342 °C; ^1H NMR δ 2.9–3.2 (m, 2 H), 3.52 (s, 4 H), 3.62 (dd, *J* = 15.5 and 5.5 Hz, 4 H), 4.04 (dd, *J* = 15.5 and 2.5 Hz, 4 H), 7.1–7.3 (m, 4 H), 7.3–7.6 (m, 4 H); MS *m/e* 442 (M^+). Anal. Calcd for $C_{25}H_{22}N_4S_2$: C, 67.81; H, 5.01; N, 12.66. Found: C, 67.58; H, 5.06; N, 12.32.

Benzo[*c*]quinoxalino[2,3-*h*]bicyclo[4.4.1]undeca-3,8-dien-11-one Ethylene Dithioacetal (6b). A mixture of **5b** (400 mg, 1.27 mmol), ethane-1,2-dithiol (1 mL), and BF_3OEt_2 (1 mL) in acetic acid (10 mL) was stirred at room temperature for 1.5 h. Precipitated **6a** was filtered, washed with a small amount of water, ethanol, and ether, and recrystallized from ethanol to give colorless plates (328 mg, 66%) of **6b**: mp 247–248 °C; ^1H NMR δ 2.8–3.0 (m, 2 H), 3.02 (dd, *J* = 16 and 6 Hz, 2 H), 3.42 (dd, *J* = 16 and 6 Hz, 2 H), 3.44 (s, 4 H), 3.6–4.1 (m, 4 H), 6.1–6.3 (m, 2 H), 6.5–6.8 (m, 2 H), 7.4–7.6 (m, 2 H), 7.6–7.7 (m, 2 H); MS *m/e* 390 (M^+), 277. Anal. Calcd for $C_{23}H_{22}N_2S_2$: C, 70.73; H, 5.68; N, 7.17. Found: C, 70.79; H, 5.72; N, 7.20.

Naphtho[2,3-*c*]quinoxalino[2′,3′-*h*]bicyclo[4.4.1]undeca-3,8-dien-11-one Ethylene Dithioacetal (6c). A mixture of **5c** (92 mg, 0.25 mmol), ethane-1,2-dithiol (0.7 mL), and BF_3OEt_2 (0.7 mL) in acetic acid (4 mL) was treated for 3 h and worked up as described above, giving **6c** (59 mg, 53%): colorless prisms (ethanol); mp 296–297 °C; ^1H NMR δ 2.8–3.1 (m, 2 H), 3.24 (dd, *J* = 15 and 6 Hz, 2 H), 3.44 (s, 4 H), 3.50 (dd, *J* = 16 and 5 Hz, 2 H), 3.87 (br d, *J* = 15 Hz, 2 H), 3.96 (ddd, *J* = 15, 2.5, and 1 Hz, 2 H), 6.8–7.0 (m, 2 H), 7.04–7.24 (m with s at 7.14, 6 H), 7.3–7.5 (m, 2 H); MS *m/e* 440 (M^+). Anal. Calcd for $C_{27}H_{24}N_2S_2$: C, 73.60; H, 5.49; N, 6.36. Found: C, 73.44; H, 5.53; N, 6.42.

Registry No. **1a**, 122761-73-3; **1b**, 122761-74-4; **1c**, 122761-75-5; **2**, 3138-86-1; **3a**, 122761-71-1; **3b**, 24790-66-7; **3c**, 122761-72-2; **4a**, 122761-76-6; **4b**, 122761-77-7; **4c**, 122761-78-8; **5a**, 122761-79-9; **5b**, 122761-80-2; **5c**, 122761-81-3; **6a**, 122761-82-4; **6b**, 122761-83-5; **6c**, 122761-84-6; dimethyl 3-oxoglutarate, 1830-54-2; *o*-xylene dibromide, 91-13-4.